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Supporting Information

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Highly Enantioselective Synthesis of 3-Substituted γ-Butenolides by Palladium-Catalyzed Kinetic Resolution of Unsymmetrical Allyl Acetates**

*Bin Mao, Yining Ji, Martín Fañanás-Mastral, Giuseppe Caroli, Auke Meetsma, and Ben L. Feringa**

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General Remarks:

Column chromatography was performed on silica gel (Silica-P flash silica gel from Silicycle, size 40-63 μm). TLC was performed on silica gel 60/Kieselguhr F254. Components were visualized by UV and stained with a solution of a mixture of $KMnO_4$ (10 g) and K_2CO_3 (10 g) in H_2O (500 mL). Mass spectra were recorded on a AEI-MS-902 mass spectrometer (EI+) or a LTQ Orbitrap XL (ESI+). ^1H- and ^{13}C-NMR were recorded on a Varian AMX400 (400 and 100.59 MHz, respectively) or a Varian VXR300 (300 and 75 MHz, respectively) using $CDCl_3$ as solvent. Chemical shift values are reported in ppm with the solvent resonance as the internal standard ($CHCl_3$: δ 7.26 for ^1H, δ 77.0 for ^{13}C). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), and integration.

Optical rotations were measured in $CHCl_3$ on a *Schmidt + Haensch* polarimeter (Polartronic MH8) with a 10 cm cell (*c* given in g/100 mL). Conversion of the reaction were determined by GC (GC, HP6890: MS HP5973) with an HP5 column (Agilent Technologies, Palo Alto, CA). The regioselectivity of the reaction were determined by GC-MS (GC, HP6890: MS HP5973) with an HP1 or HP5 column (Agilent Technologies, Palo Alto, CA). Enantioselectivities were determined by HPLC analysis using a Shimadzu LC-10AD*VP* HPLC equipped with a Shimadzu SPD-M10A*VP* diode array detector or by capillary GC analysis (HP 6890, Chiraldex G-TA column (30 m x 0.25 mm), Chiraldex B-PM column (30 m x 0.25 mm), or CP-Cyclodextrin-β-2,3,6-M-19 column (50 m x 0.25 mm)) using flame ionization detector.

All reactions were carried out under a nitrogen atmosphere using oven dried glassware and using standard Schlenk techniques. All solvents were reagent grade and were dried and distilled prior to use, if necessary. Tetrahydrofuran and diethylether were distilled over Na/benzophenone. Toluene and dichloromethane were distilled over calcium hydride. All the ligands, palladium catalysts and silyl enol ether **2a** were purchased from Acros and Sigma-Aldrich. Substrates **1a,**[1] **1b**[2] and silyl enol ether **2b**[3] were prepared following literature procedures.

Racemic products were synthesized by reaction of silyl enol ether **2** (1.2 mmol) with the corresponding allylic substrates (0.6 mmol) at room temperature in CH_2Cl_2 in the presence of $Pd_2(dba)_3{\cdot}CHCl_3$ (5 mol%) and PPh_3 (15 mol%).

General procedure for the synthesis of racemic allylic acetates (1c-l):

Allylic alcohols were synthesized by reaction of the α,β-unsaturated aldehydes with the corresponding Grignard reagent at 0 °C in CH_2Cl_2 or reduction from corresponding ketone in the presence of sodium borohydride. The alcohols were used directly for the following reactions without further purification. Acetic anhydride (2 equiv) was added at 0 ºC to a solution of allylic alcohol (1.0 equiv), NEt_3 (2.0 equiv) and DMAP (10 mol%) in dry DCM (0.2 M). The reaction mixture was allowed to warm to room temperature and stirred at this temperature until the total consumption of the starting material. The reaction was quenched with saturated brine and the organic layer was separated. The aqueous layer was extracted with diethyl ether and the combined organics were washed with saturated aqueous $NaHCO_3$, dried over Na_2SO_4 and the solvent was removed under *vaccum*. Futher purification was achieved by Kugelrohr distillation.

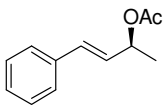
General procedure for Pd-catalyzed kinetic resolution of allylic substrates 1 with silyl enol ethers 2:

To a dry Schlenk tube containing $Pd_2(dba)_3{\cdot}CHCl_3$ (0.0175 mmol, 18 mg) was added a solution of Trost ligand (*R,R*)-**L1** (0.0525 mmol, 38 mg) in dry DCM (1 mL). After stirring at room temperature for 15 min, a solution of

trimethylsilyloxyfuran (0.35 mmol, 60 μL) in dry DCM (0.5 mL) was added dropwise. After the mixture had been stirred for another 15 min at room temperature, a solution of acetate (0.35 mmol) and *n*-dodecane (30 μL, internal standard) in dry DCM (0.5 mL) were added via syringe pump over 0.5 h maintaining the temperature below 0 ºC. Reaction progress was followed by GC and GC-MS. After completion of the reaction, the solvent was removed under *vacuum*. The crude product was purified by flash chromatography on silica gel using different mixtures of Pentane/Et_2O as eluents. Toluene:Et_2O 95:5 was used for TLC to distinguish the resulted regioisomers. The absolute configuration depicted for all the products is assumed to be the same to that of **3c**, as determined by X-ray crystallography.

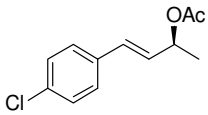
Characterization of Recovered Acetates and Products

(−)-(*S*)-(*E*)-4-phenylbut-3-en-2-yl acetate ((*S*)-1c)



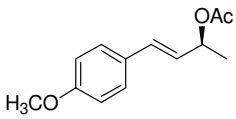
Colourless oil. Yield: 43%. ee: 99%. $[\alpha]_D^{20}$ = -96.5 (*c* 0.8, $CHCl_3$). [lit.[4] (*R* isomer, 94% ee): $[\alpha]_D^{20}$ = +120.2 (*c* 1.14, $CHCl_3$)]. The physical data were identical in all respects to those previously reported.[5] Ee was determined by chiral HPLC or chiral GC analysis, Chiralpak OB-H (Heptane/*i*-Propanol = 98/2, 0.5 mL/min, 210 nm), retention times: t_R (major) 20.81 min, t_R (minor) 23.33 min. Chiral CP-Cyclodextrin-*β*-2,3,6-M-19 column (50 m x 0.25 mm), (initial temp. 50 °C, gradient 10 °C/min to 160 °C, 160 °C isothermic for 15 min), retention time: t_R (major) 24.53 min.

(−)-(*S*)-(*E*)-4-(4-chlorophenyl)but-3-en-2-yl acetate ((*S*)-1d)



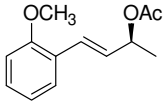
Colourless oil. Yield: 42%. ee: 99%. $[\alpha]_D^{20}$ = -116 (*c* 2.8, $CHCl_3$). [lit.[4] (*R* isomer, 94% ee): $[\alpha]_D^{20}$ = +132.3 (*c* 0.92, $CHCl_3$)]. The physical data were identical in all respects to those previously reported.[5] Ee was determined by chiral HPLC, Chiralpak AD-H (Heptane/*i*-Propanol = 98/2, 0.5 mL/min, 210 nm), retention time: t_R (major) 12.57 min.

(−)-(*S*)-(*E*)-4-(4-methoxyphenyl)but-3-en-2-yl acetate ((*S*)-1e)



Colourless oil. Yield: 38%. ee: 99%. $[\alpha]_D^{20}$ = -85 (*c* 2.8, $CHCl_3$). [lit.[4] (*R* isomer, > 99% ee): $[\alpha]_D^{20}$ = +125.9 (*c* 1.10, $CHCl_3$)]. The physical data were identical in all respects to those previously reported.[5] Ee was determined by chiral HPLC, Chiralpak OB-H (Heptane/*i*-Propanol = 95/5, 0.5 mL/min, 262 nm), retention time: t_R (major) 43.49 min.

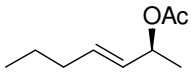
(−)-(*S*)-(*E*)-4-(2-methoxyphenyl)but-3-en-2-yl acetate ((*S*)-1f)



Colourless oil. Yield: 44%. ee: 94%. $[\alpha]_D^{20}$ = -108 (*c* 3.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.32 – 7.16 (m, 1H), 6.98 – 6.88 (m, 2H), 6.86 (d, *J* = 8.2 Hz, 1H), 6.22 (dd, *J* = 16.1, 6.8 Hz, 1H), 5.64 – 5.40 (m, 1H), 3.85 (s, 3H), 2.07 (s, 3H), 1.42 (t, *J* = 5.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.34, 156.86, 129.31, 128.93, 126.96, 126.45, 125.27, 120.56, 110.84,

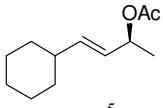
71.54, 55.41, 21.44, 20.43. HRMS (ESI+, *m/z*): calcd for $C_{15}H_{17}O_3$ $[M+H]^+$: 245.11722, found 245.11578. Ee was determined by chiral HPLC, Chiralpak OJ-H (Heptane/*i*-Propanol = 98/2, 0.5 mL/min, 210 nm), retention times: t_R (major) 22.53 min, t_R (minor) 19.14 min.

(−)-(*S*)-(*E*)-hept-3-en-2-yl acetate ((*S*)-1g)



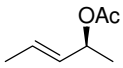
Colourless oil. Yield: 36%. ee: 94%. $[\alpha]_D^{20}$ = -55 (*c* 1.8, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.74 – 5.64 (m, 1H), 5.45 (ddt, *J* = 15.4, 6.8, 1.3 Hz, 1H), 5.30 (dq, *J* = 6.5 Hz, 1H), 2.03 (s, 3H), 2.01 – 1.95 (m, 2H), 1.45 – 1.33 (m, 2H), 1.28 (d, *J* = 6.4 Hz, 2H), 0.87 (dt, *J* = 13.9, 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.64, 133.14, 129.58, 71.17, 34.18, 22.07, 21.42, 20.37, 13.58. HRMS (ESI+, *m/z*): calcd for $C_{11}H_{17}O_2$ $[M+H]^+$: 181.12231, found 181.12086. Ee was determined by chiral GC analysis, Chiraldex G-TA column (30 m x 0.25 mm), (initial temp. 50 °C, gradient 10 °C/min to 170 °C), retention times: t_R (major) 25.74 min, t_R (minor) 26.88 min.

(−)-(*S*)-(*E*)-4-cyclohexylbut-3-en-2-yl acetate ((*S*)-1h)



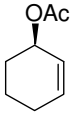
Colourless oil. Yield: 44%. ee: 92%. $[\alpha]_D^{20}$ = -13 (*c* 2.8, $CHCl_3$). [lit.[4] (*R* isomer, 95% ee): $[\alpha]_D^{20}$ = +71.1 (*c* 0.97, $CHCl_3$)]. The physical data were identical in all respects to those previously reported.[5] Ee was determined by chiral GC analysis, Chiraldex B-PM column (30 m x 0.25 mm), (initial temp. 50 °C, gradient 2 °C/min to 100 °C, 100 °C isothermic for 30 min, gradient 5 °C/min to 160 °C), retention times: t_R (major) 61.78 min, t_R (minor) 62.85 min.

(−)-(*S*)-(*E*)-pent-3-en-2-yl acetate ((*S*)-1i)



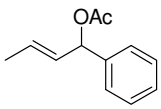
Colourless oil. Yield: 18%. ee: 91%. $[\alpha]_D^{20}$ = -94 (*c* 0.1, $CHCl_3$). [lit.[5] (*S* isomer): $[\alpha]_D^{20}$ = -65.5 (*c* 1.2, EtOH)]. The physical data were identical in all respects to those previously reported.[6] Ee was determined by chiral GC analysis, Chiraldex G-TA column (30 m x 0.25 mm), (initial temp. 50 °C, gradient 10 °C/min to 170 °C), retention times: t_R (major) 8.63 min, t_R (minor) 10.02 min.

(+)-(*R*)-cyclohex-2-en-1-yl acetate ((*R*)-1j)



Colourless oil. Yield: 33%. ee: 99%. $[\alpha]_D^{20}$ = +202 (*c* 0.9, $CHCl_3$). [lit.[6] (*R* isomer, 99% ee): $[\alpha]_D^{23}$ = +199.0 (*c* 2.40, CH_2Cl_3)]. The physical data were identical in all respects to those previously reported.[7] Ee was determined by chiral GC analysis, Chiraldex G-TA column (30 m x 0.25 mm), (initial temp. 60 °C, gradient 5 °C/min to 170 °C), retention times: t_R (major) 27.89 min, t_R (minor) 28.97 min.

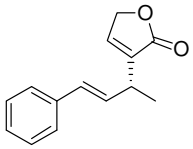
(*E*)-1-phenylbut-2-en-1-yl acetate (1l)



Pale yellow oil. Yield: 55%. ee: 8%. $[\alpha]_D^{20}$ = 0.1 (*c* 1.0, $CHCl_3$). The physical data were identical in all respects to those previously reported.[7] Ee was determined by chiral GC analysis, Chiraldex

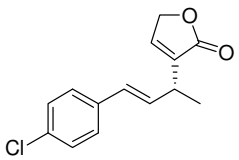
B-PM column (30 m x 0.25 mm), (initial temp. 50 °C, gradient 2 °C/min to 100 °C, 100 °C isothermic for 30 mins, gradient 5 °C/min to 160 °C), retention times: t_R (major) 60.58 min, t_R (minor) 60.89 min.

(−)-(*R*)-(*E*)-3-(4-phenylbut-3-en-2-yl)furan-2(5H)-one (3c)



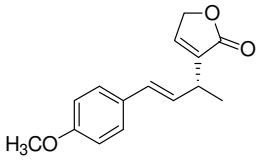
Colourless oil. Yield: 47%. ee: 99%. $[\alpha]_D^{20}$ = -17.5 (*c* 3.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.18 (m, 5H), 7.14 (dd, *J* = 3.0, 1.5 Hz, 1H), 6.48 (d, *J* = 15.9 Hz, 1H), 6.28 (dd, *J* = 15.9, 7.3 Hz, 1H), 4.76 (t, *J* = 1.5 Hz, 2H), 3.45 (dd, *J* = 11.1, 4.0 Hz, 1H), 1.39 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.27, 143.84, 137.51, 136.85, 130.74, 130.02, 128.40, 127.30, 126.10, 77.32, 33.77, 18.60. HRMS (ESI+, *m/z*): calcd for $C_{14}H_{15}O_2$ $[M+H]^+$: 215.10666, found 215.10579. Ee was determined by chiral HPLC, Chiralpak AS-H (Heptane/*i*-Propanol = 97/3, 0.5 mL/min, 254 nm), retention times: t_R (major) 29.51 min, t_R (minor) 25.34 min.

(−)-(*R*)-(*E*)-3-(4-(4-chlorophenyl)but-3-en-2-yl)furan-2(5H)-one (3d)



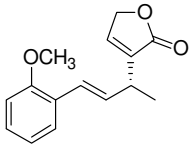
Colourless oil. Yield: 47%. ee: 99%. $[\alpha]_D^{20}$ = -6.1 (*c* 2.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 1H), 7.15 (dd, *J* = 3.0, 1.6 Hz, 1H), 6.43 (d, *J* = 15.3 Hz, 1H), 6.24 (dd, *J* = 15.9, 7.3 Hz, 1H), 4.78 (bs, 2H), 3.45 (dd, *J* = 14.2, 7.1 Hz, 1H), 1.38 (d, *J* = 7.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.24, 143.84, 137.48, 135.44, 132.93, 131.47, 128.96, 128.59, 127.40, 70.08, 33.85, 18.58. HRMS (ESI+, *m/z*): calcd for $C_{14}H_{14}ClO_2$ $[M+H]^+$: 249.06768, found 249.06563. Ee was determined by chiral HPLC, Chiralpak AD-H (Heptane/*i*-Propanol = 98/2, 0.5 mL/min, 210 nm), retention time: t_R (major) 49.45 min. In accordance with the results obtained in the kinetic resolution of **1c**, the absolute configuration of this compound is assumed to be (*R*), analogous to compound **3c**.

(−)-(*R*)-(*E*)-3-(4-(4-methoxyphenyl)but-3-en-2-yl)furan-2(5H)-one (3e)



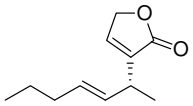
Colourless oil. Yield: 46%. ee: 99%. $[\alpha]_D^{20}$ = -4.1 (*c* 2.3, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.6 Hz, 2H), 7.14 (dd, *J* = 3.0, 1.7 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.42 (d, *J* = 15.8 Hz, 1H), 6.13 (dd, *J* = 15.9, 7.3 Hz, 1H), 4.78 (t, *J* = 1.7 Hz, 2H), 3.80 (s, 3H), 3.43 (m, 1H), 1.37 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.40, 159.05, 143.60, 138.01, 129.72, 129.52, 128.62, 127.33, 113.91, 70.06, 55.26, 33.85, 18.80. HRMS (ESI+, *m/z*): calcd for $C_{15}H_{17}O_3$ $[M+H]^+$: 245.11722, found 245.11543. Ee was determined by chiral HPLC, Chiralpak OD (Heptane/*i*-Propanol = 99/1, 1 mL/min, 254 nm), retention time: t_R (major) 41.76 min. In accordance with the results obtained in the kinetic resolution of **1c**, the absolute configuration of this compound is assumed to be (*R*), analogous to compound **3c**.

(+)-(*R*)-(*E*)-3-(4-(2-methoxyphenyl)but-3-en-2-yl)furan-2(5H)-one (3f)



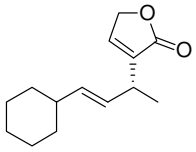
Colourless oil. Yield: 41%. ee: 99%. $[\alpha]_D^{20}$ = +3.1 (*c* 2.6, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.21 (td, *J* = 8.3, 1.7 Hz, 1H), 7.14 (d, *J* = 1.4 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 6.81 (d, *J* = 16.0 Hz, 1H), 6.30 (dd, *J* = 16.0, 7.3 Hz, 1H), 4.77 (s, 2H), 3.84 (s, 3H), 3.57 – 3.36 (m, 1H), 1.39 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.39, 156.50, 143.70, 138.05, 131.34, 128.44, 126.59, 125.95, 124.88, 120.57, 110.81, 70.05, 55.41, 34.30, 18.82. HRMS (ESI+, *m/z*): calcd for $C_{15}H_{17}O_3$ $[M+H]^+$: 245.11722, found 245.11578. Ee was determined by chiral HPLC, Chiralpak AD-H (Heptane/*i*-Propanol = 98/2, 0.5 mL/min, 210 nm), retention times: t_R (major) 39.78 min. In accordance with the results obtained in the kinetic resolution of **1c**, the absolute configuration of this compound is assumed to be (*R*), analogous to compound **3c**.

(−)-(*R*)-(*E*)-3-(hept-3-en-2-yl)furan-2(5H)-one (3g)



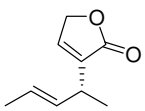
Colourless oil. Yield: 39%. ee: 99%. $[\alpha]_D^{20}$ = -21 (*c* 2.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, *J* = 1.4 Hz, 1H), 5.50 (dd, *J* = 10.3, 5.8 Hz, 2H), 4.75 (t, *J* = 1.7 Hz, 2H), 3.28 – 3.11 (m, 1H), 2.06 – 1.87 (m, 2H), 1.42 – 1.29 (m, 2H), 1.25 (d, *J* = 7.0 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.52, 143.29, 138.43, 130.97, 70.00, 34.47, 33.54, 22.42, 18.98, 13.61. HRMS (ESI+, *m/z*): calcd for $C_{11}H_{17}O_2$ $[M+H]^+$: 181.12231, found 181.12086. Ee was determined by chiral HPLC, Chiralpak OB-H (Heptane/*i*-Propanol = 98/2, 0.5 mL/min, 210 nm), retention times: t_R (major) 29.07 min, t_R (minor) 27.68 min. In accordance with the results obtained in the kinetic resolution of **1c**, the absolute configuration of this compound is assumed to be (*R*), analogous to compound **3c**.

(−)-(*R*)-(*E*)-3-(4-cyclohexylbut-3-en-2-yl)furan-2(5H)-one (3h)



Colourless oil. Yield: 36%. ee: 99%. $[\alpha]_D^{20}$ = -13 (*c* 2.8, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.05 (t, *J* = 1.5 Hz, 1H), 5.45 (p, *J* = 15.6 Hz, 2H), 4.75 (t, *J* = 1.7 Hz, 2H), 3.19 (dd, *J* = 9.4, 3.9 Hz, 1H), 2.03 – 1.84 (m, 1H), 1.76 – 1.56 (m, 5H), 1.24 (d, *J* = 7.0 Hz, 6H), 1.13 – 0.99 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.50, 143.23, 138.57, 137.01, 128.29, 69.96, 40.49, 33.50, 33.00, 26.13, 26.00, 18.99. HRMS (ESI+, *m/z*): calcd for $C_{14}H_{21}O_2$ $[M+H]^+$: 221.15361, found 221.15185. Ee was determined by chiral HPLC, Chiralpak OB-H (Heptane/*i*-Propanol = 98/2, 0.5 mL/min, 210 nm), retention times: t_R (major) 24.45 min, t_R (minor) 21.89 min. In accordance with the results obtained in the kinetic resolution of **1c**, the absolute configuration of this compound is assumed to be (*R*), analogous to compound **3c**.

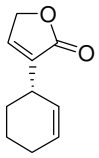
(−)-(*R*)-(*E*)-3-(pent-3-en-2-yl)furan-2(5H)-one (3i)



Colourless oil. Yield: 25%. ee: 88%. $[\alpha]_D^{20}$ = -27 (*c* 1.0, CHCl3). ^1H NMR (400 MHz, $CDCl_3$) δ 7.05-7.06 (m, 1H), 5.59 – 5.42 (m, 2H), 4.76 (bs, 2H), 3.26 – 3.14 (m, 1H), 1.67 (d, *J* = 4.9 Hz, 3H), 1.24 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.53, 143.33, 138.29, 131.99, 125.61, 69.99, 33.51, 18.89, 17.82. HRMS (ESI+, *m/z*): calcd for $C_9H_{13}O$ $[M+H]^+$: 153.09101, found 153.09053. Ee was

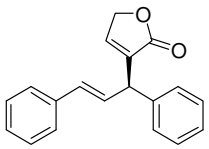
determined by chiral HPLC, Chiralpak OB-H (Heptane/*i*-Propanol = 98/2, 0.5 mL/min, 254 nm), retention times: t_R (major) 40.03 min, t_R (minor) 44.57 min. In accordance with the results obtained in the kinetic resolution of **1c**, the absolute configuration of this compound is assumed to be (*R*), analogous to compound **3c**.

(−)-(*S*)-3-(cyclohex-2-en-1-yl)furan-2(5H)-one (3j)



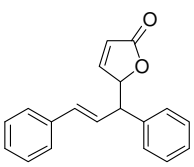
Colourless oil. Yield: 35%. ee: 99%. $[\alpha]_D^{20}$ = -47.2 (*c* 1.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 1.6 Hz, 1H), 5.87 (m, 1H), 5.63 (m, 1H), 4.77 (t, *J* = 1.7 Hz, 2H), 3.19 (s, 1H), 2.00 (m, 3H), 1.67 – 1.47 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.66, 144.59, 137.73, 129.52, 126.69, 70.10, 32.17, 27.25, 24.86, 19.93. HRMS (ESI+, *m/z*): calcd for $C_{10}H_{13}O_2$ $[M+H]^+$: 165.09101, found 165.08968. Ee was determined by chiral HPLC, Chiralpak OB-H (Heptane/*i*-Propanol = 98/2, 0.5 mL/min, 210 nm), retention time: t_R (major) 54.16 min. In accordance with the results obtained in the kinetic resolution of **1c**, the absolute configuration of this compound is assumed to be (*S*).

(−)-(*R*)-(*E*)-3-(1,3-diphenylallyl)furan-2(5H)-one (3k)



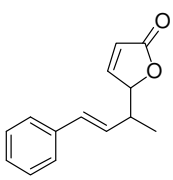
Pale yellow oil. Yield: 55%. ee: 92%. $[\alpha]_D^{20}$ = -51 (*c* 0.7, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.21 (m, 10H), 7.18 (d, *J* = 1.3 Hz, 1H), 6.52 (dd, *J* = 15.9, 7.1 Hz, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 4.84 (dt, *J* = 4.0, 1.7 Hz, 2H), 4.67 (d, *J* = 7.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.73, 146.03, 139.93, 136.64, 136.33, 132.04, 128.78, 128.71, 128.52, 128.11, 127.65, 127.17, 126.36, 70.06, 45.13. HRMS (ESI+, *m/z*): calcd for $C_{19}H_{16}O_2Na$ $[M+Na]^+$: 299.10425, found: 299.10376. Ee was determined by chiral HPLC, Chiralpak AD-H (Heptane/*i*-Propanol = 95/5, 0.5 mL/min, 210 nm), retention times: t_R (major) 16.52 min, t_R (minor) 23.32 min. In accordance with the results obtained in the kinetic resolution of **1c**, the absolute configuration of this compound is assumed to be (*R*), analogous to compound **3c**.

(+)-(*E*)-5-(1,3-diphenylallyl)furan-2(5H)-one (4k)



Pale yellow oil. Yield: 13%. $[\alpha]_D^{20}$ = +42 (*c* 0.7, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 5.8, 1.5 Hz, 1H), 7.42 – 7.11 (m, 10H), 6.60 (d, *J* = 15.8 Hz, 1H), 6.41 (dd, *J* = 15.8, 8.5 Hz, 1H), 6.08 (dd, *J* = 5.8, 2.0 Hz, 1H), 5.53 – 5.20 (m, 1H), 3.88 (dd, *J* = 8.5, 6.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.48, 138.07, 136.45, 133.68, 128.83, 128.60, 128.20, 127.89, 127.54, 126.41, 126.30, 122.83, 85.35, 52.30. HRMS (ESI+, *m/z*): calcd for $C_{19}H_{17}O_2$ $[M+H]^+$: 277.12231, found: 277.12022.

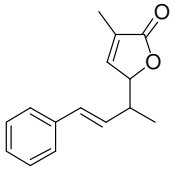
(+)-(*E*)-5-(4-phenylbut-3-en-2-yl)furan-2(5H)-one (4l)



Colourless oil. Yield: 16%. ee: 34%. $[\alpha]_D^{20}$ = +40 (*c* 1.9, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 5.8, 1.5 Hz, 1H), 7.39 – 7.28 (m, 5H), 6.49 (d, *J* = 16.0 Hz, 1H), 6.16 (dd, *J* = 5.8,

2.0 Hz, 1H), 6.09 (dd, *J* = 15.9, 7.7 Hz, 1H), 5.11 – 5.01 (m, 1H), 2.87 (dd, *J* = 11.9, 6.7 Hz, 1H), 1.18 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.95, 154.60, 136.57, 132.19, 128.58, 128.18, 127.70, 126.24, 122.64, 86.39, 39.88, 15.29. HRMS (ESI+, *m/z*): calcd for $C_{14}H_{15}O_2$ $[M+H]^+$: 215.10666, found: 215.06861. Ee was determined by chiral HPLC, Chiralpak AD-H (Heptane/*i*-Propanol = 98/2, 0.5 mL/min, 254 nm), retention times: t_R (major) 40.03 min, t_R (minor) 44.57 min.

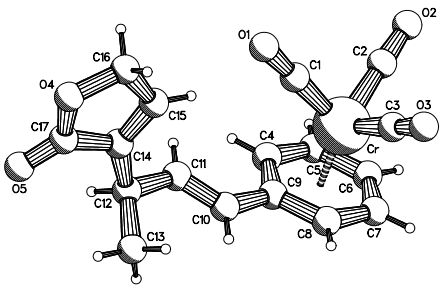
(−)-(*E*)-3-methyl-5-(4-phenylbut-3-en-2-yl)furan-2(5H)-one (5)



Colourless oil. Yield: 32%. ee: 86%. $[\alpha]_D^{20}$ = -22 (*c* 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.10 (m, 5H), 6.85 – 6.70 (m, 1H), 5.72 (ddd, *J* = 15.3, 7.5, 1.6 Hz, 1H), 5.64 – 5.49 (m, 1H), 5.12 – 4.98 (m, 1H), 3.40 (t, *J* = 7.5 Hz, 1H), 1.86 (s, 3H), 1.76 – 1.65 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.06, 147.59, 139.56, 130.65, 128.96, 128.72, 128.13, 127.24, 83.53, 52.75, 29.67, 18.05, 10.59. HRMS (ESI+, *m/z*): calcd for $C_{15}H_{17}O_2$ $[M+H]^+$: 229.12231, found 229.12047. Ee was determined by chiral HPLC, Chiralpak AD-H (Heptane/*i*-Propanol = 99/1, 0.5 mL/min, 210 nm), retention times: t_R (major) 36.74 min, t_R (minor) 28.67 min.

Preparation and Characterization of Chromium Complex

A solution of **3c** (0.37 mmol) and $Cr(CO)_3(CH_3CN)_3$ (0.41 mmol) in THF (5 mL) was refluxed for 24 h, and then the solvents were removed under *vacuum*. The crude product was purified by flash chromatography on silica gel using Pentane/Et_2O as eluents. Recrystallization from Pentane/EtOAc gave orange crystals, m.p. = 107 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 22.7 Hz, 1H), 6.24 (dd, *J* = 15.9, 7.0 Hz, 1H), 6.03 (d, *J* = 15.9 Hz, 1H), 5.48 – 5.34 (m, 3H), 5.24 (t, *J* = 5.8 Hz, 1H), 4.79 (s, 2H), 3.65 – 3.32 (m, 1H), 1.37 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 235.23, 173.16, 144.48, 136.94, 133.91, 126.61, 105.67, 93.20, 90.84, 90.60, 90.11, 70.23, 33.60, 18.35.



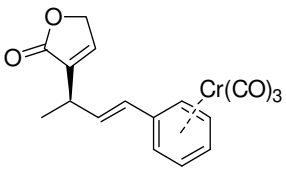


Figure S1. ORTEP Diagram of Chromium Complex of **3c**.

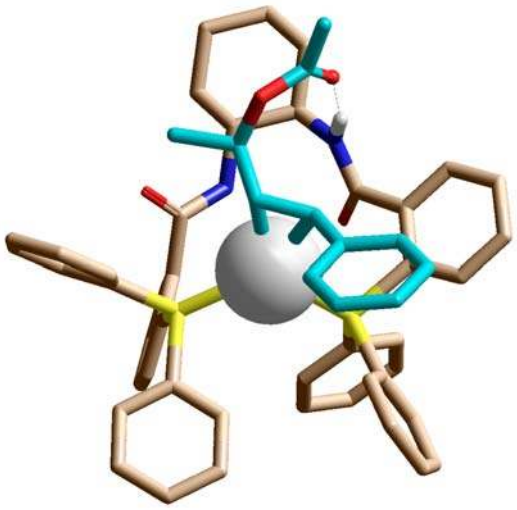
Computational Details

To the optimized structure of ligand (*R,R*)-**L1**,[8] the (*R*) or (*S*) enantiomer of **1c** was added and a conformational analysis was carried out with the Hyperchem software package[9] at the PM3 level of theory. The 6 lowest energy conformations were refined at the DFT B3LYP level employing a mixed basis set (in particular the LANL2DZ

basis,[10] as downloaded from the BSE website,[11] was used for the Pd and the 6-31G(d,p) for all the other elements). For these DFT calculations, the Firefly QC package (partially based on the GAMESS US source code)[12] was used.[13] Finally, the conformation with the lowest DFT energy was considered for further discussions. On the basis of the lowest DFT energy conformation of the Pd/(*R*,*R*)-**L1**/(*R*)-**1c** complex, products **3** and **4** were modeled in the same way.

Density Functional Theory (DFT) Calculations

Optimized structure of Pd/(*R*,*R*)-**L1**/(*R*)-**1c**



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O	-1.12910000	-3.21370000	2.32260000
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N	0.34170000	-3.95260000	0.74690000
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C	-1.29450000	-5.54980000	-2.32740000
C	-0.26530000	-4.74500000	-1.51260000
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C	1.17970000	-2.77080000	2.70860000
C	1.22080000	-1.45340000	3.22580000
C	2.24160000	-1.13860000	4.13530000
C	3.19390000	-2.08290000	4.52730000
C	3.15990000	-3.36770000	3.99390000
C	2.15430000	-3.70190000	3.08720000
C	1.28920000	-1.66500000	-3.11970000
C	1.88980000	-0.42390000	-2.78400000
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C	1.20440000	-1.01880000	-5.46910000
C	0.94740000	-1.93710000	-4.45070000
C	3.68480000	-0.78400000	-0.49080000
C	4.02610000	-0.78330000	0.86740000
C	5.21930000	-1.36310000	1.30240000
C	6.08610000	-1.95530000	0.38420000

C	5.75220000	-1.96560000	-0.97180000
C	4.56110000	-1.38500000	-1.40640000
C	2.83020000	1.82780000	-1.19230000
C	1.95000000	2.91760000	-1.10690000
C	2.41730000	4.22790000	-1.22750000
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C	4.19720000	2.08690000	-1.39110000
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C	1.15990000	2.99410000	5.12360000
C	1.96860000	3.79280000	4.31140000
C	2.20430000	3.41490000	2.98970000
C	1.63530000	2.24390000	2.48470000
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C	0.02380000	-3.29260000	1.88940000
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H	3.96120000	-1.80400000	5.24500000
H	3.90190000	-4.10750000	4.28130000
H	2.10310000	-4.70670000	2.67830000
H	2.58640000	1.44350000	-3.59870000
H	2.02950000	0.91950000	-5.92880000
H	0.93860000	-1.25560000	-6.49550000
H	0.49540000	-2.89490000	-4.68940000
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H	5.46150000	-1.35790000	2.36140000
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H	0.96610000	3.28350000	6.15340000

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H	2.82210000	4.03070000	2.34150000
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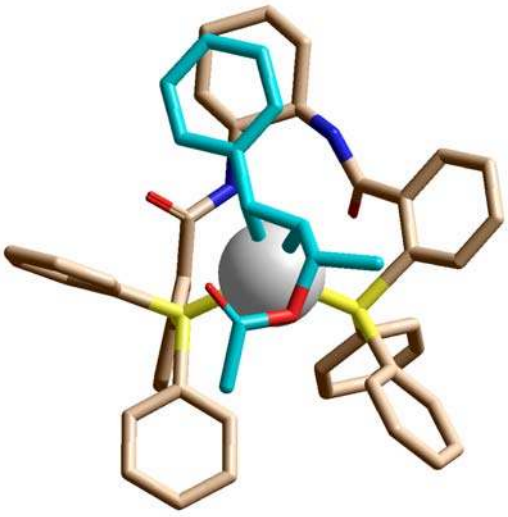
Optimized structure of Pd/(*R,R*)-**L1**/(*S*)-**1c**



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C	2.78220000	-1.95660000	4.76320000
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C	3.93980000	-0.88600000	1.04620000
C	5.05590000	-1.54210000	1.56970000
C	5.94940000	-2.19080000	0.71810000
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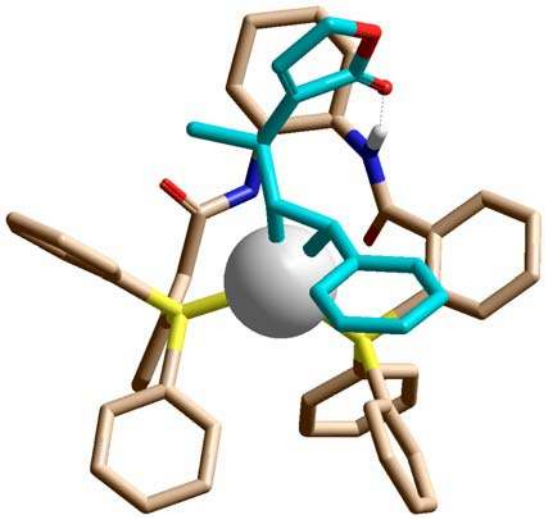
Optimized structure of the 3-substituted product **3c** coordinated with complex Pd/(*R*,*R*)-**L1**



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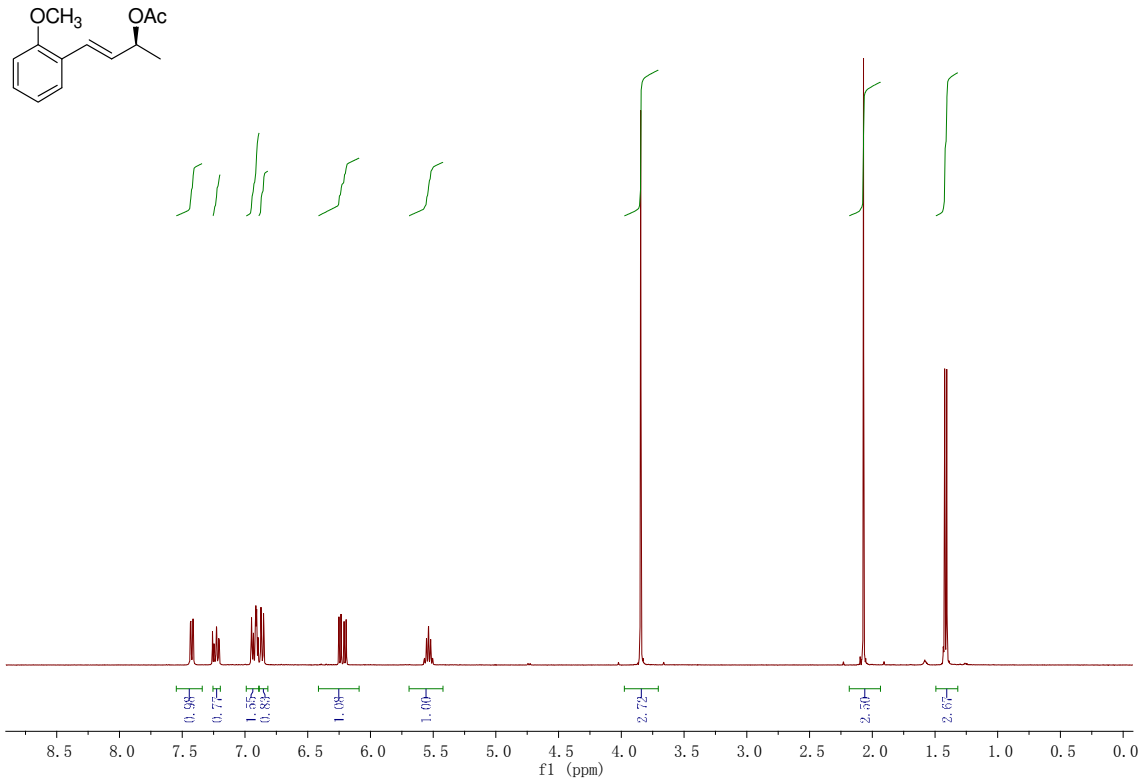
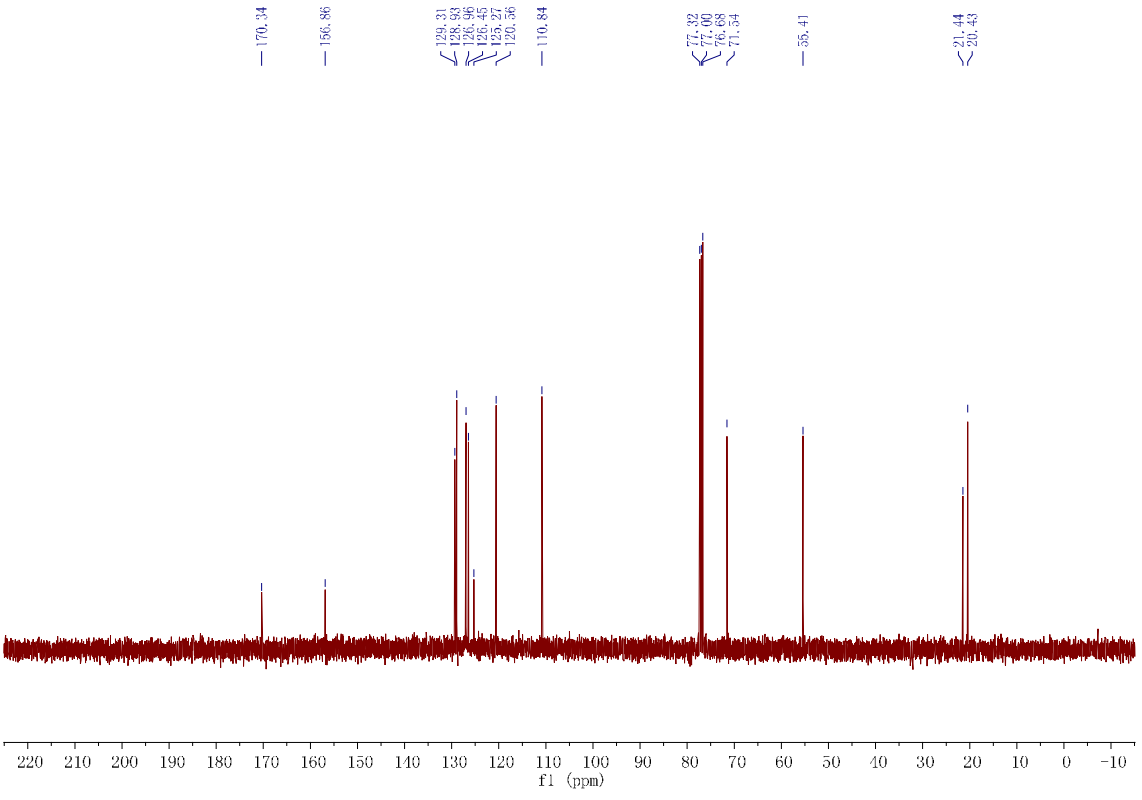
NMR Spectra

(-)-(*S*)-(*E*)-4-(2-methoxyphenyl)but-3-en-2-yl acetate ((*S*)-1f)

^{1}H-NMR

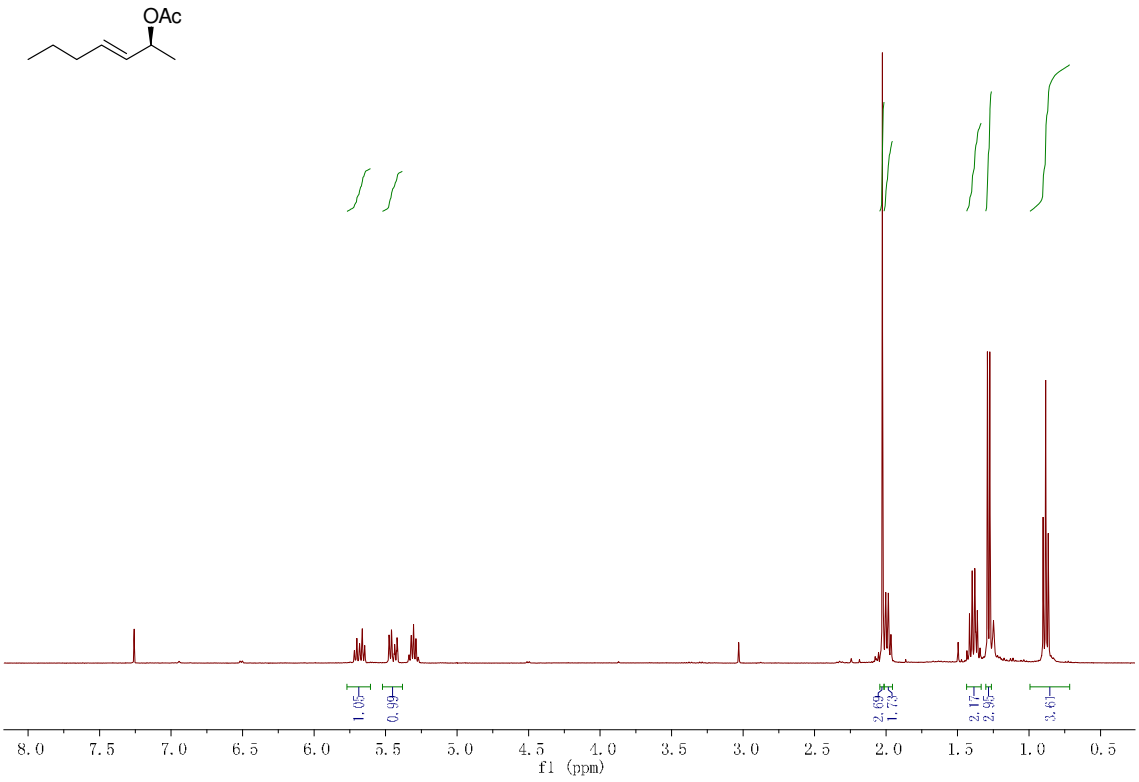


^{13}C-NMR



(-)-(*S*)-(*E*)-hept-3-en-2-yl acetate ((*S*)-1g)

^{1}H-NMR



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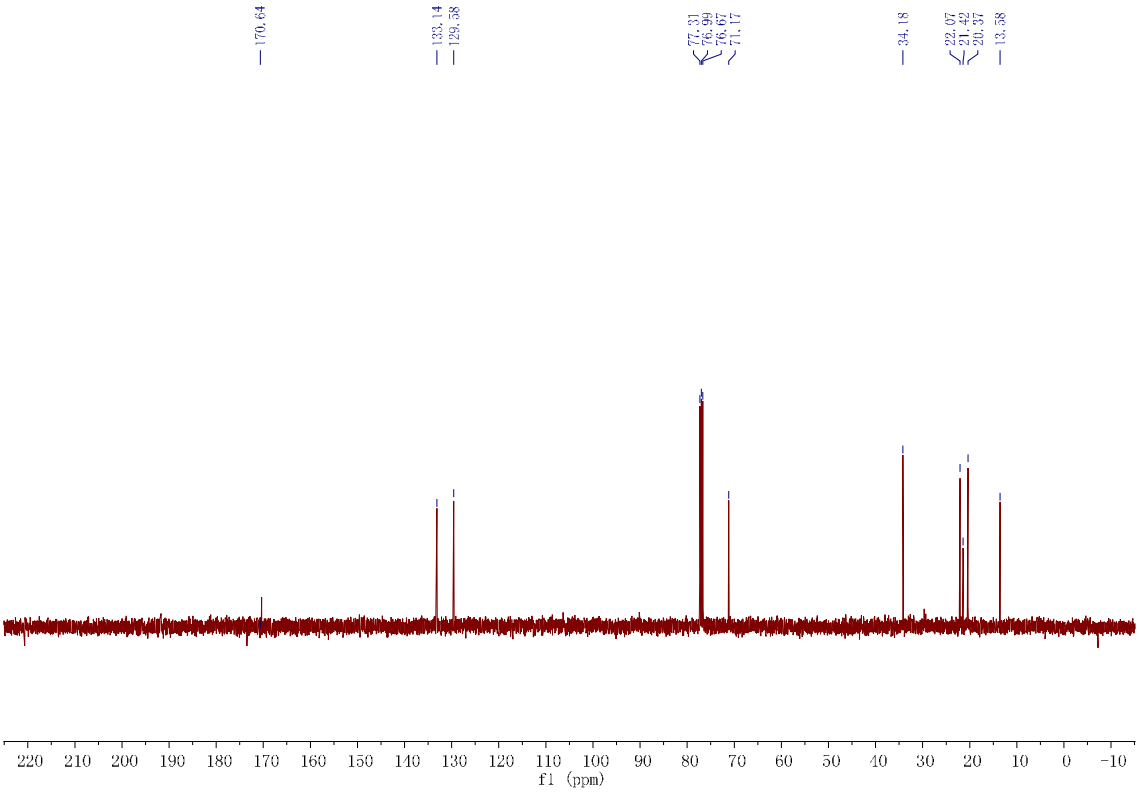

(-)-(*R*)-(*E*)-3-(4-phenylbut-3-en-2-yl)furan-2(5H)-one (3c)

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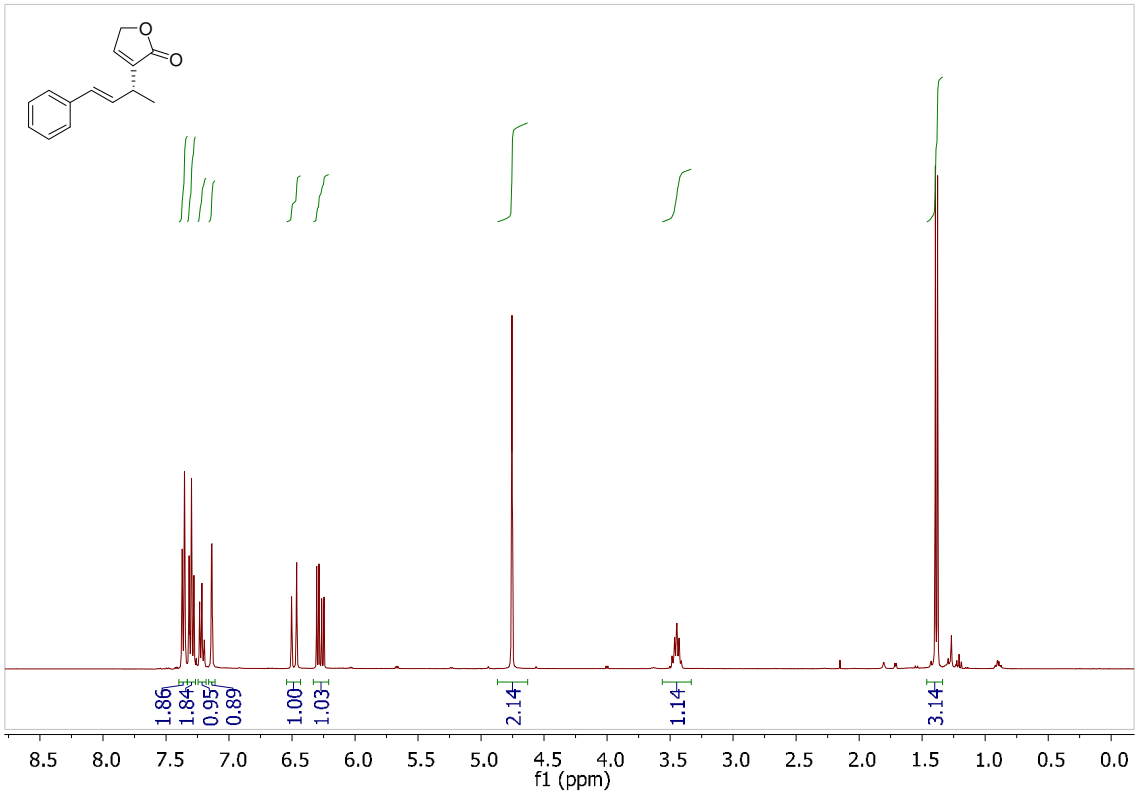

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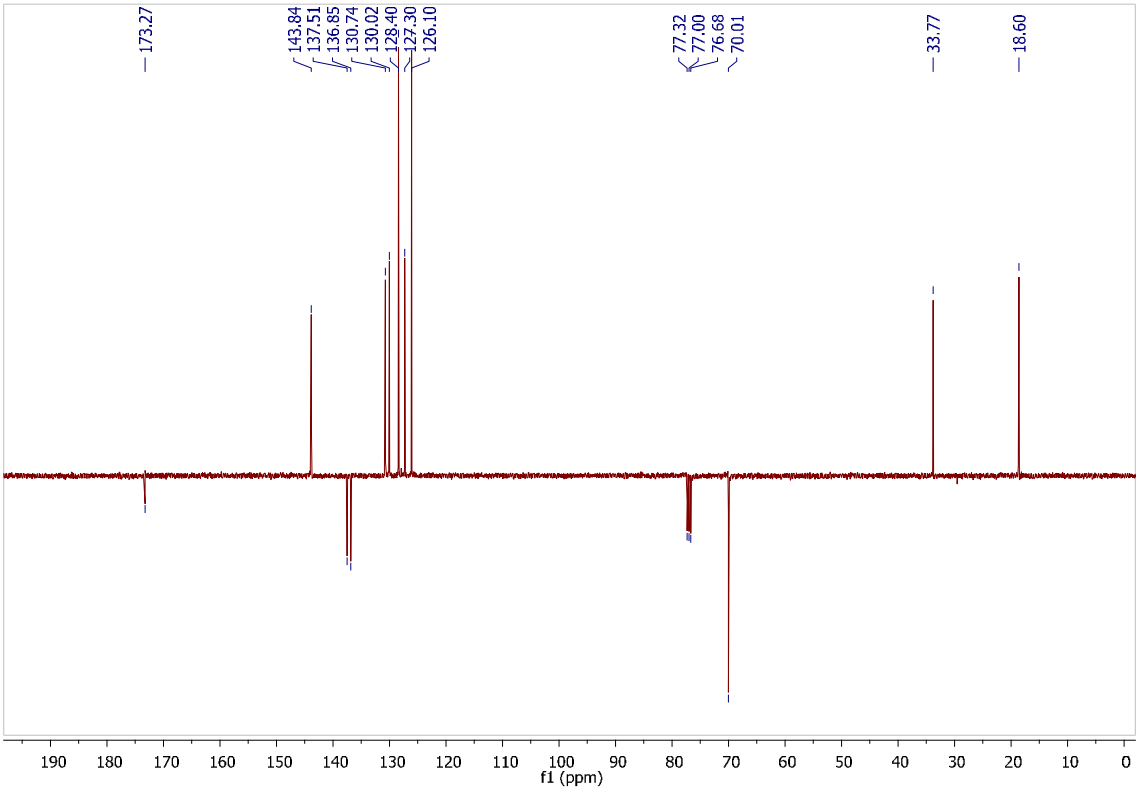

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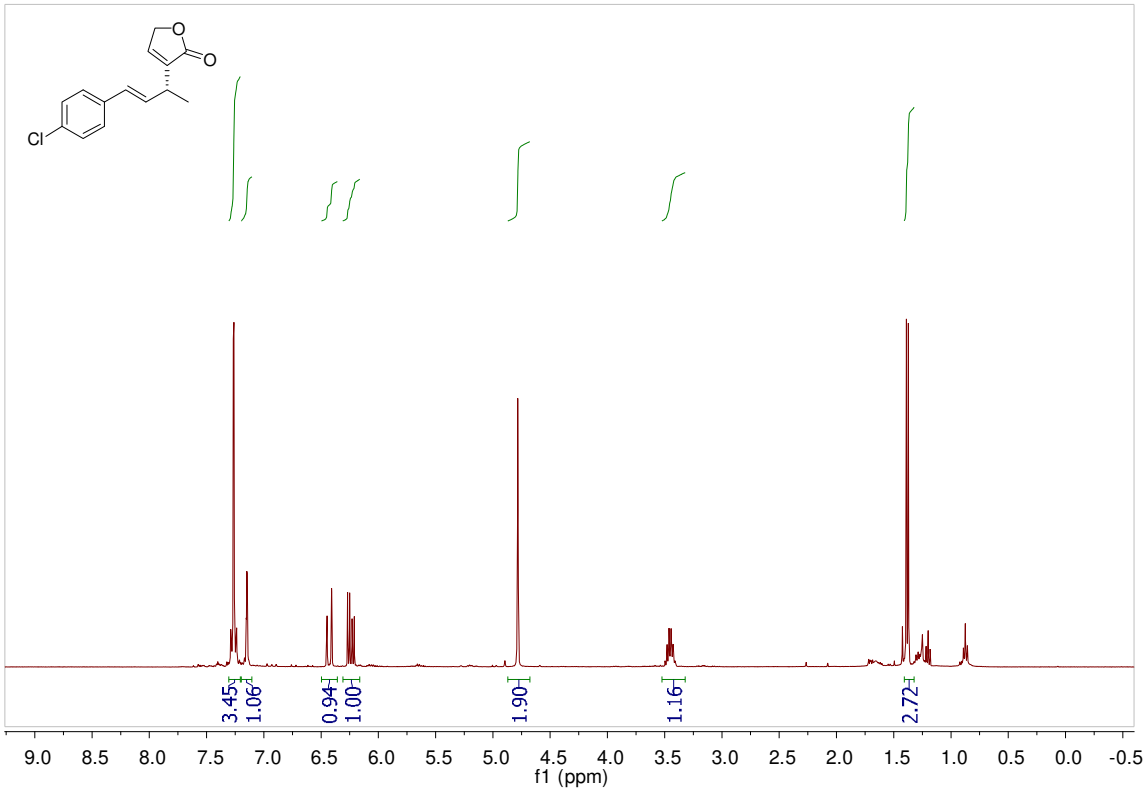
^{1}H-NMR



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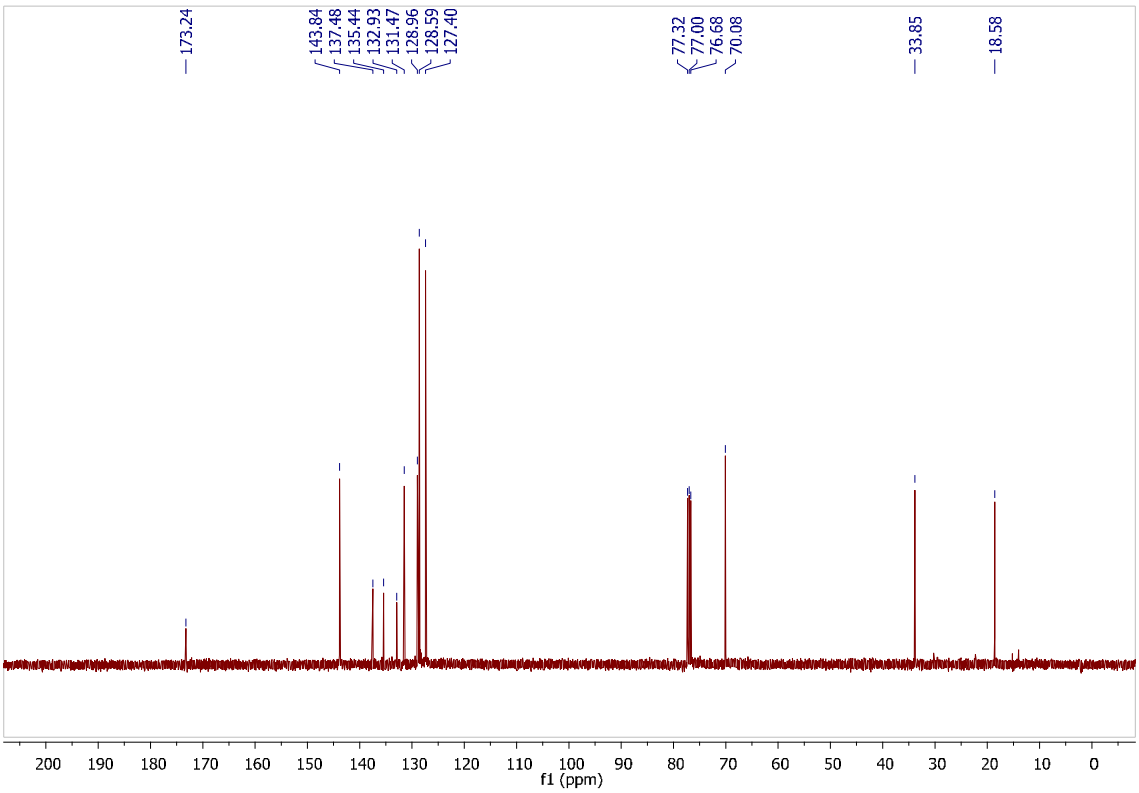

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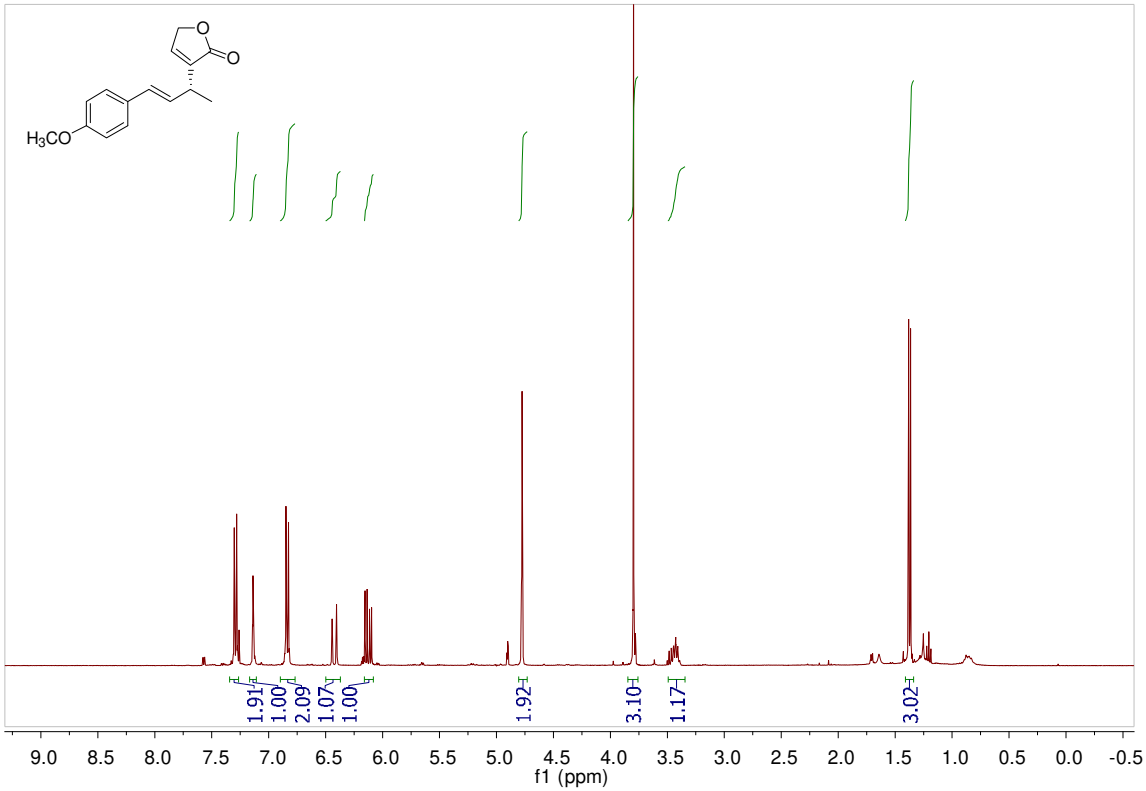
^{1}H-NMR



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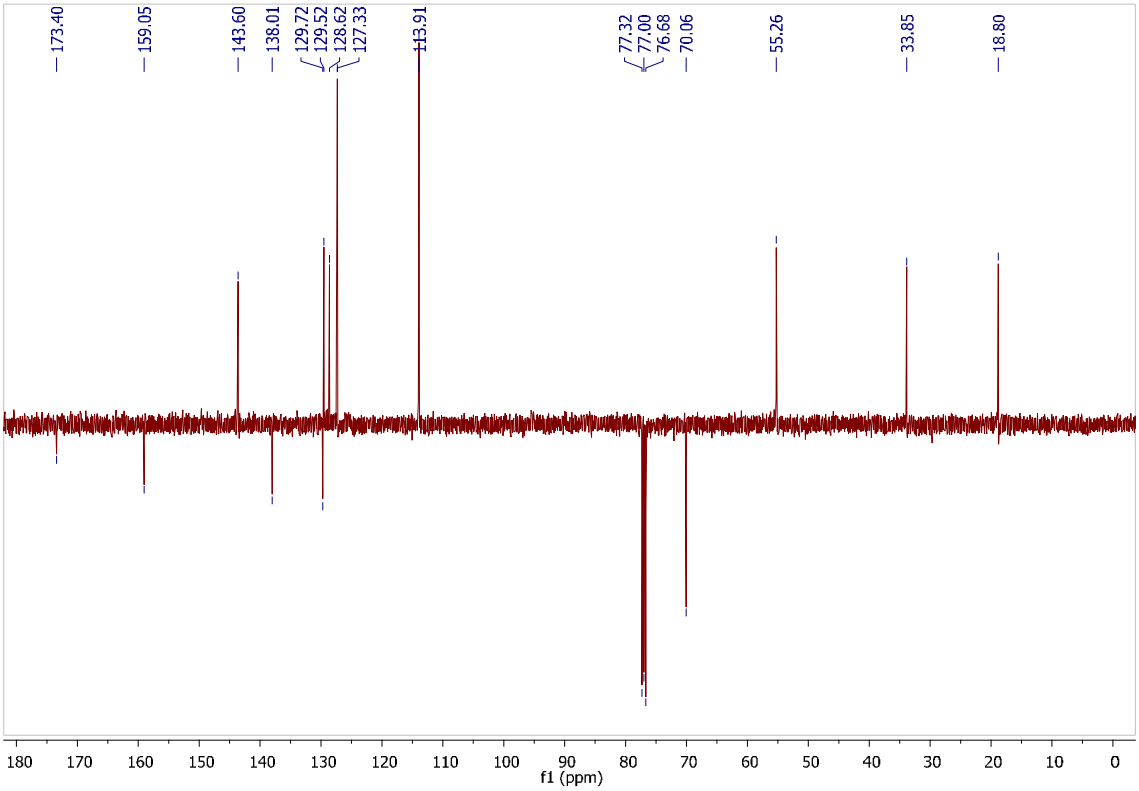

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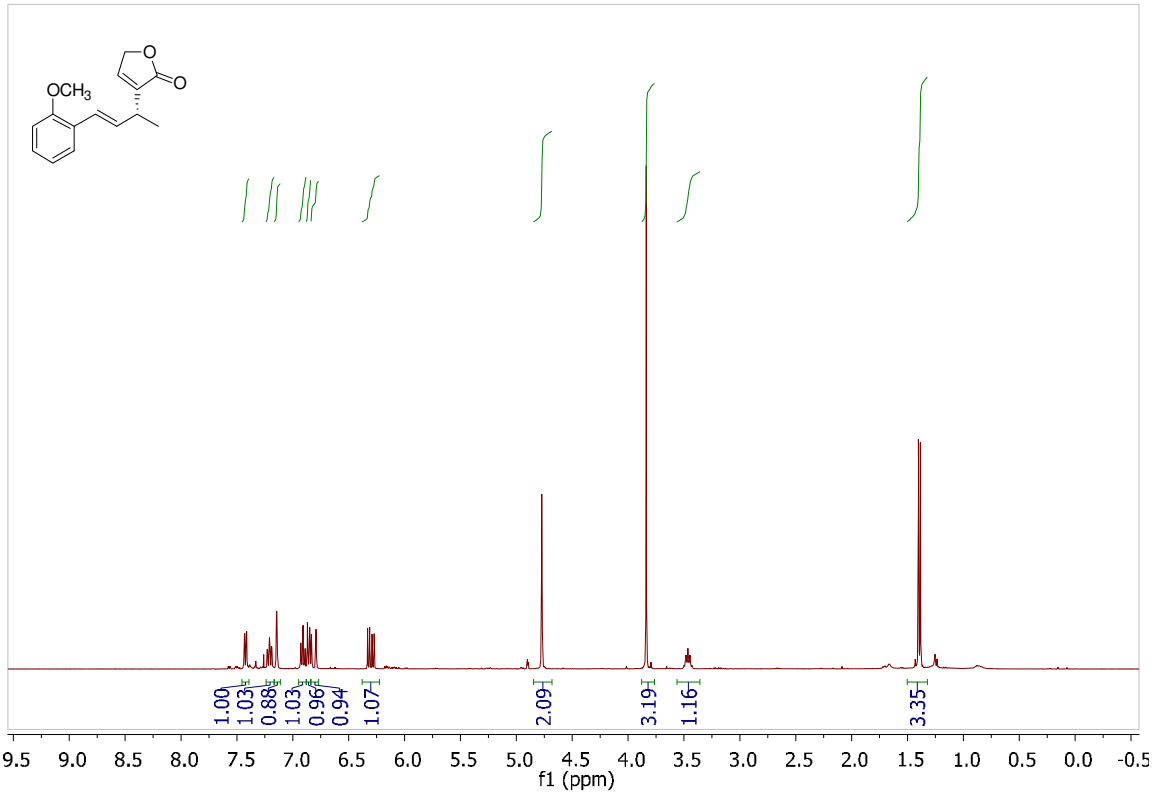
^{1}H-NMR



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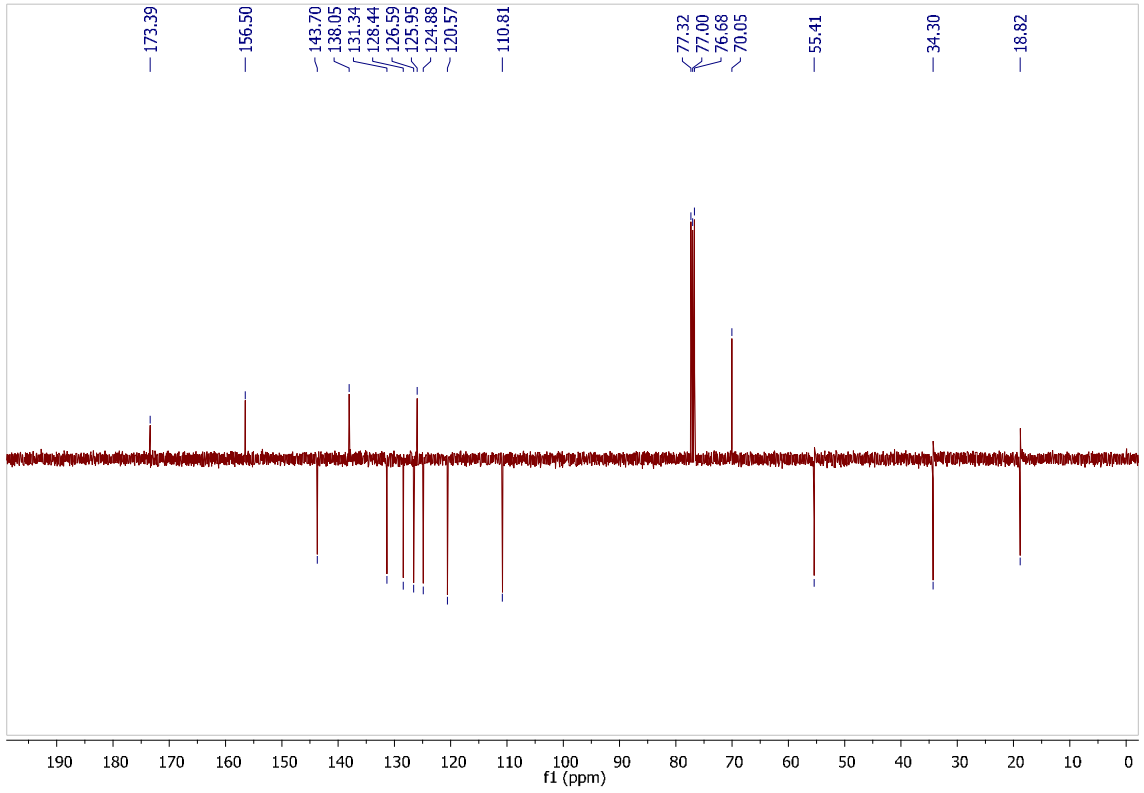
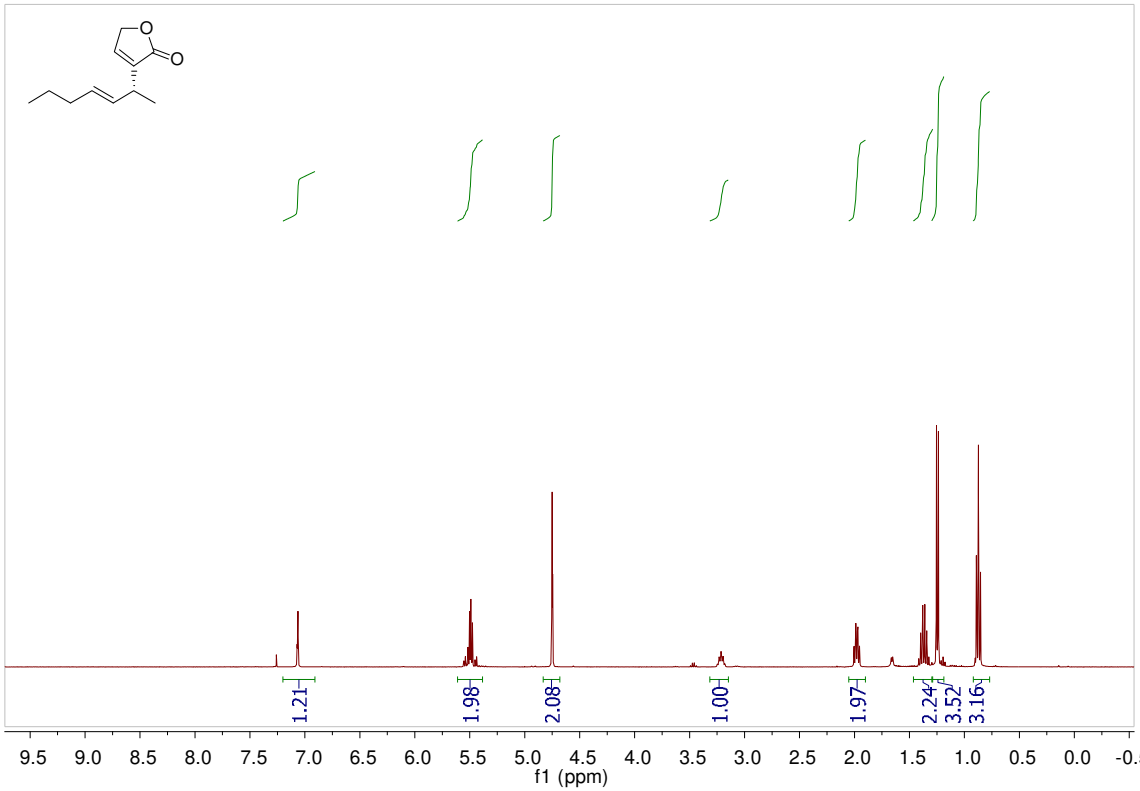


(-)-(*R*)-(*E*)-3-(hept-3-en-2-yl)furan-2(5H)-one (3g)

^{1}H-NMR



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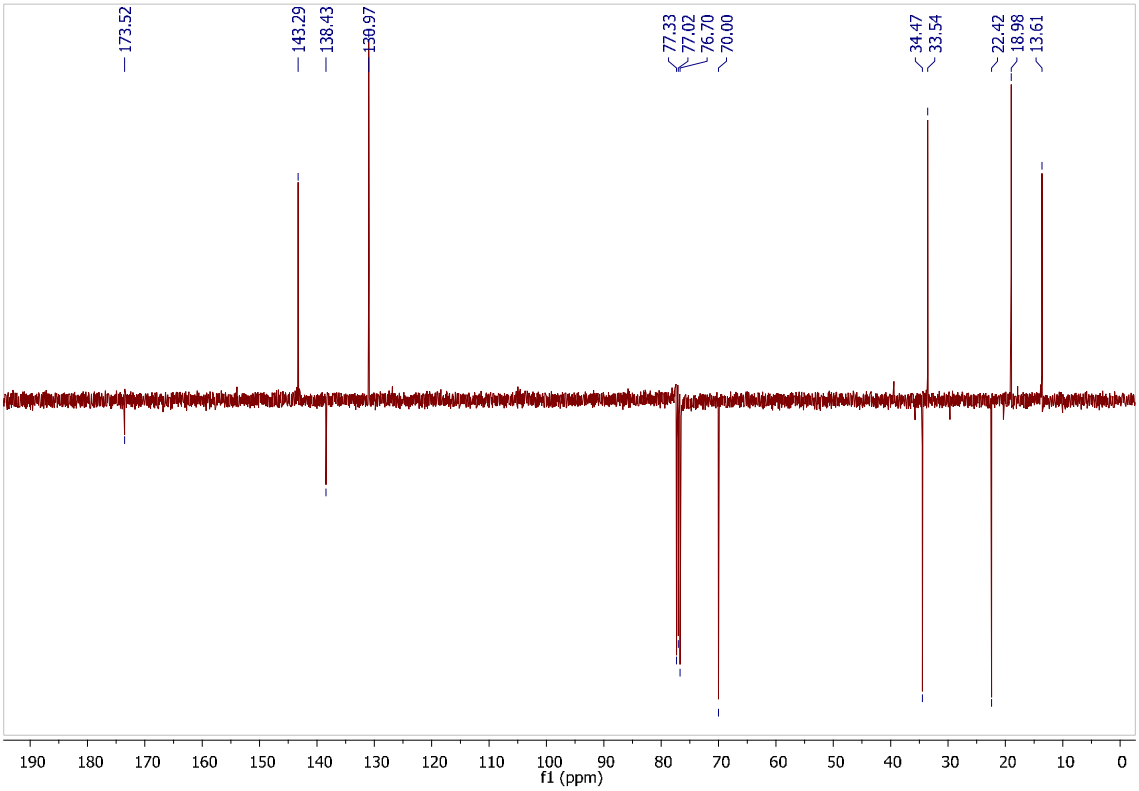
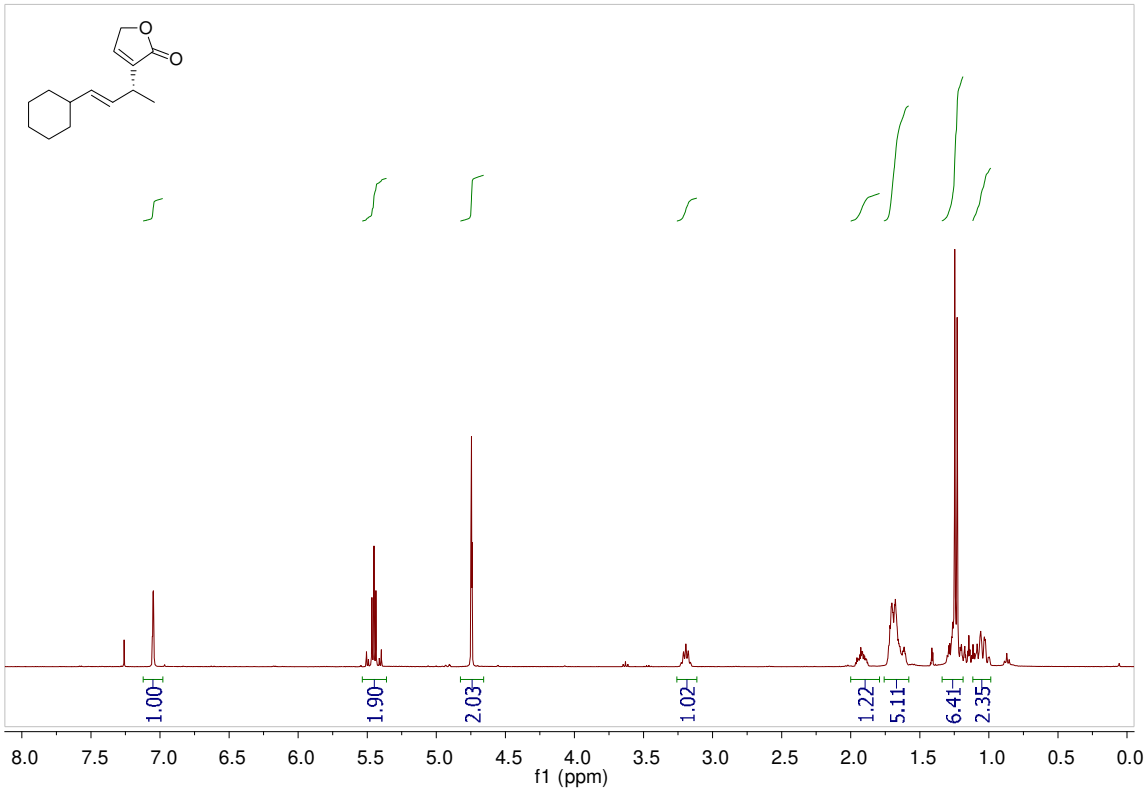


(-)-(*R*)-(*E*)-3-(4-cyclohexylbut-3-en-2-yl)furan-2(5H)-one (3h)

^{1}H-NMR



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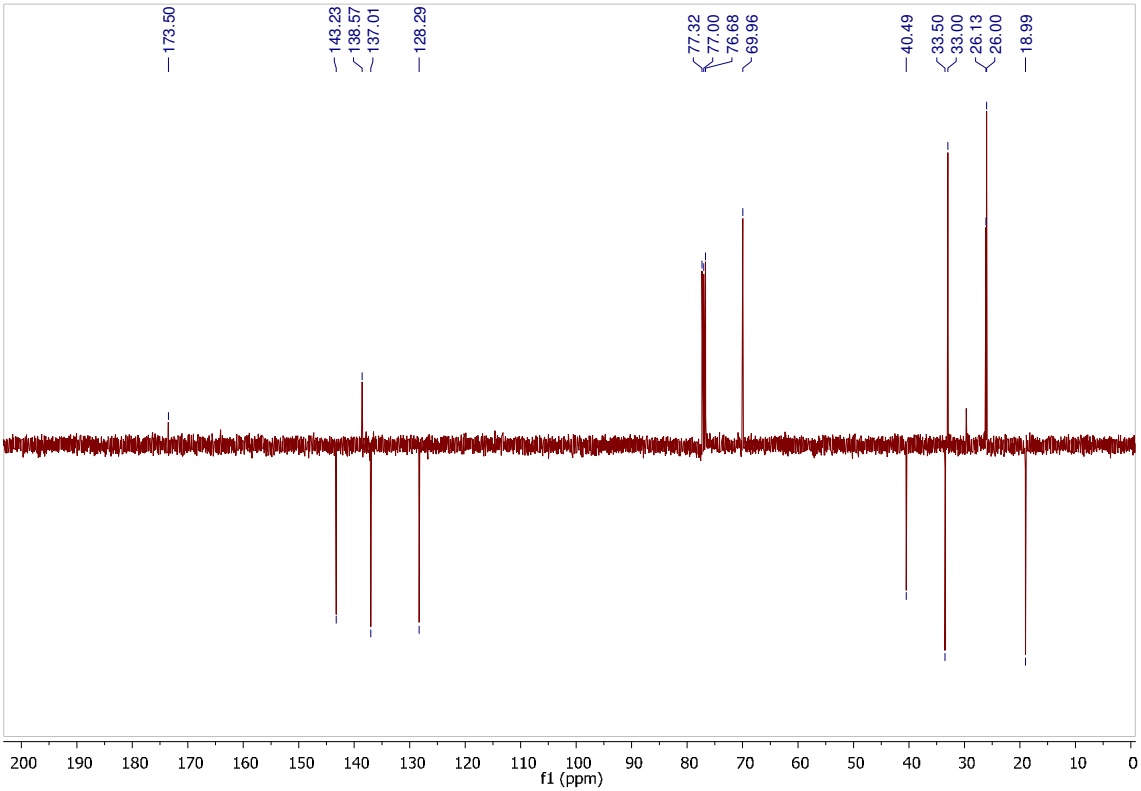
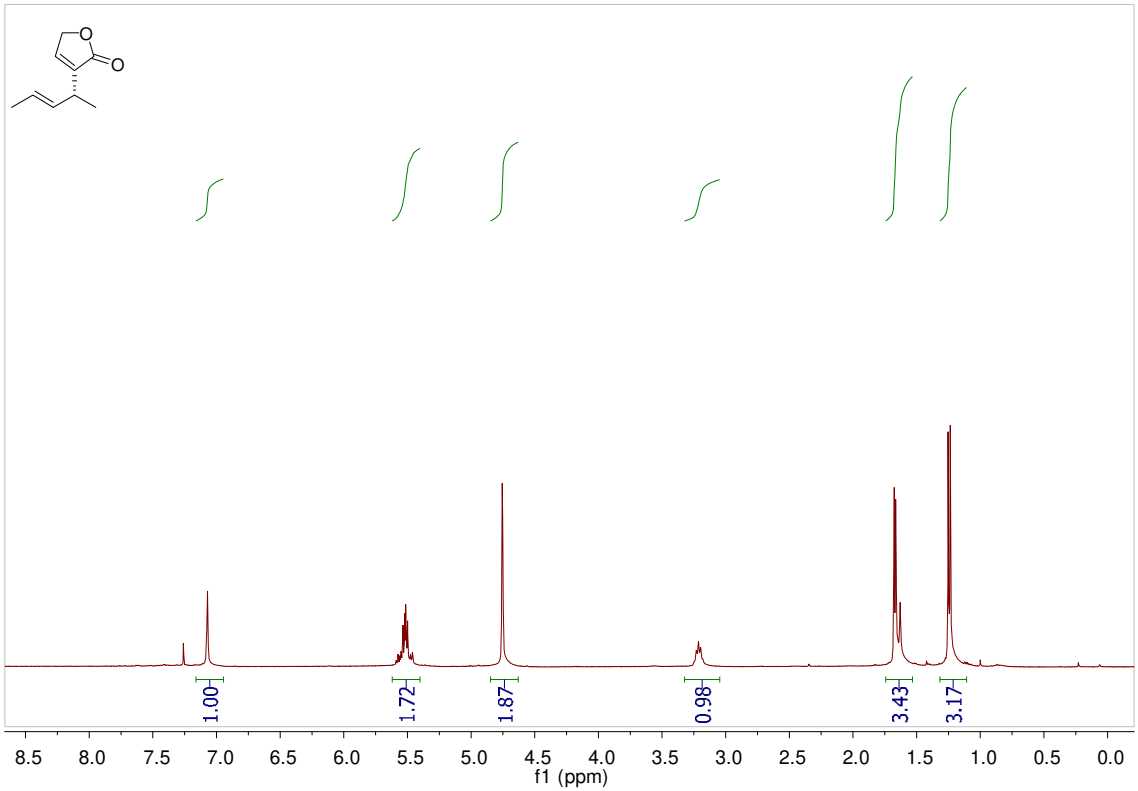
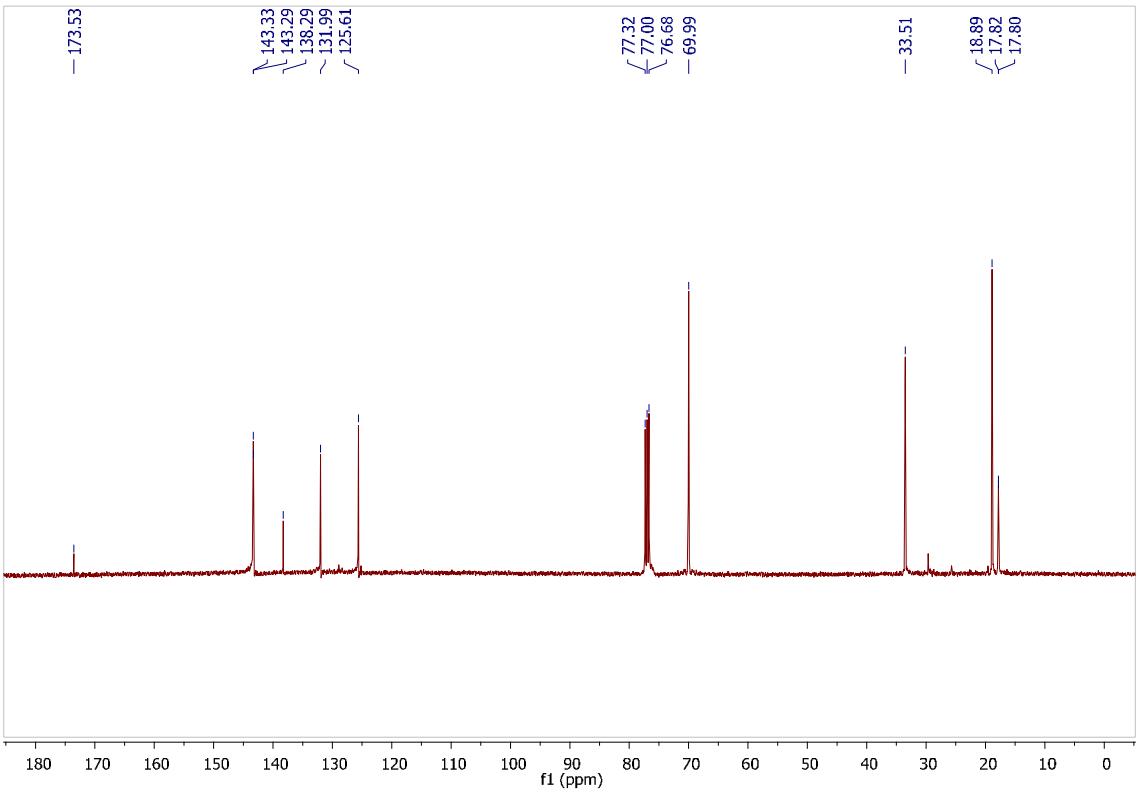


(-)-(*R*)-(*E*)-3-(pent-3-en-2-yl)furan-2(5H)-one (3i)

^{1}H-NMR

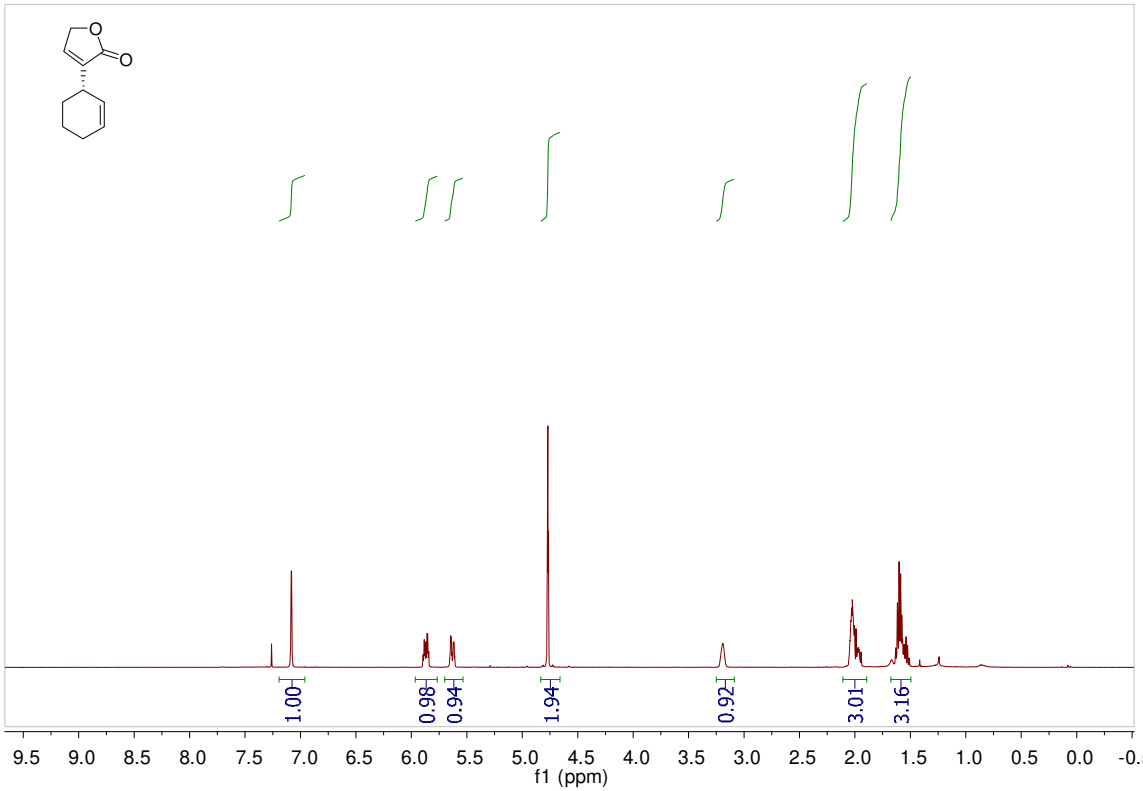


^{13}C-NMR

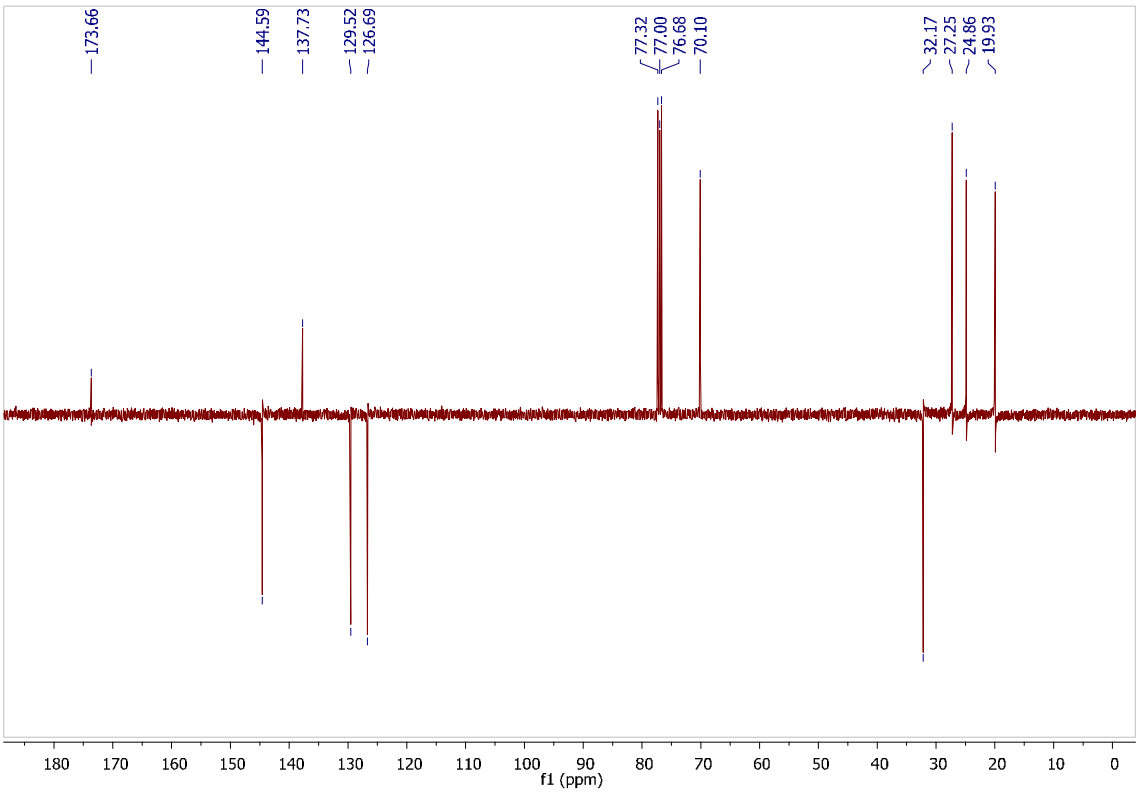


(-)-(*S*)-3-(cyclohex-2-en-1-yl)furan-2(5H)-one (3j)

^{1}H-NMR

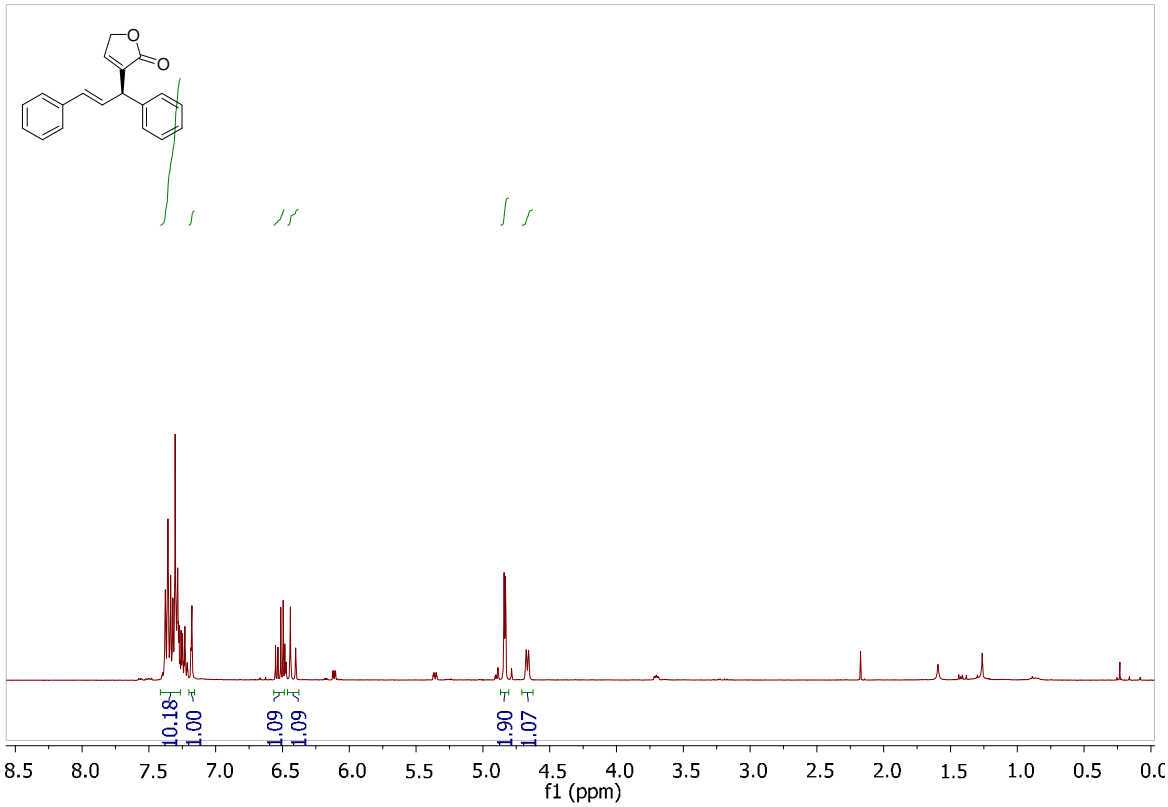


APT

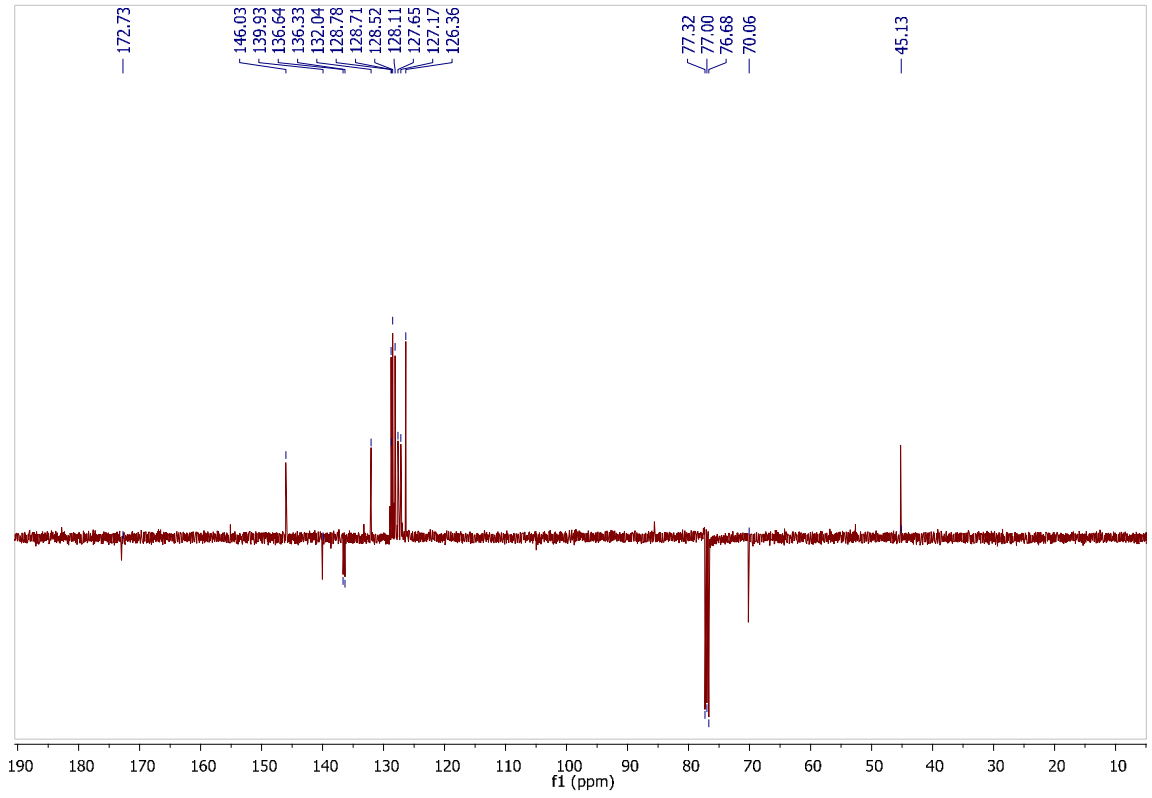


(-)-(*R*)-(*E*)-3-(1,3-diphenylallyl)furan-2(5H)-one (3k)

^{1}H-NMR

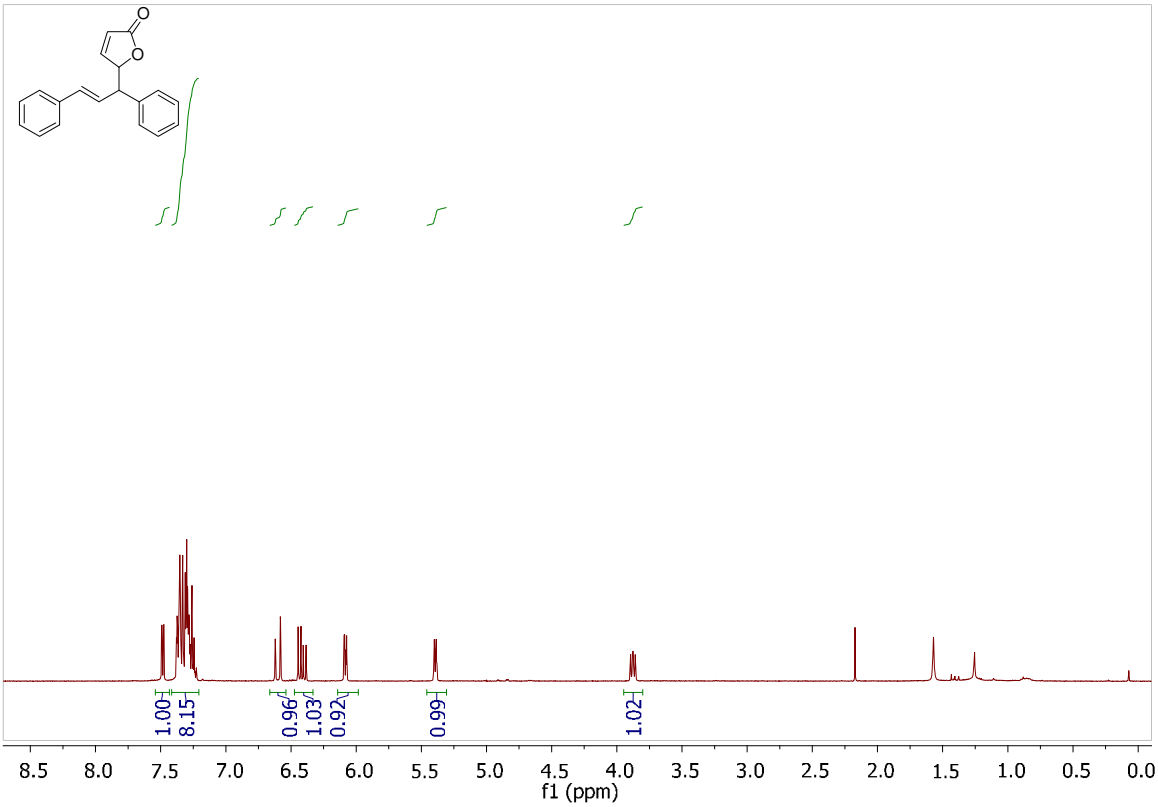


APT



(+)-(*E*)-5-(1,3-diphenylallyl)furan-2(5H)-one (4k)

^{1}H-NMR



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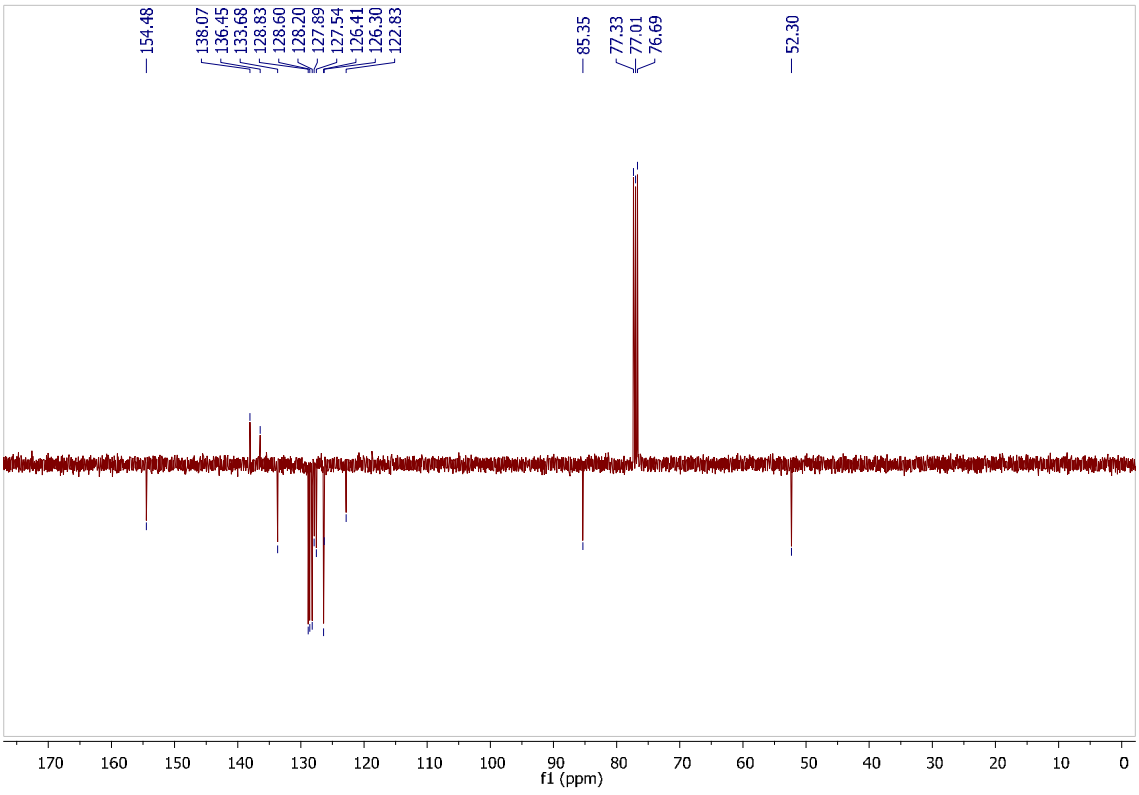
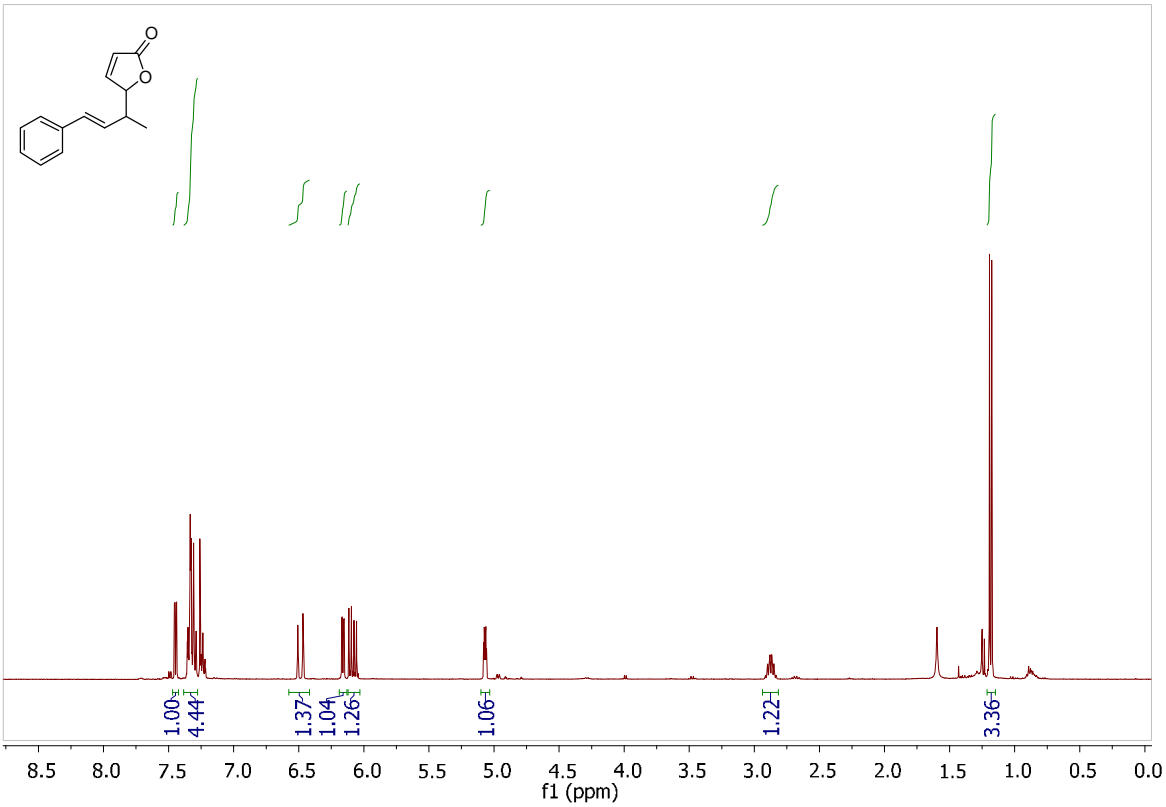


(+)-(*E*)-5-(4-phenylbut-3-en-2-yl)furan-2(5H)-one (4l)

^{1}H-NMR



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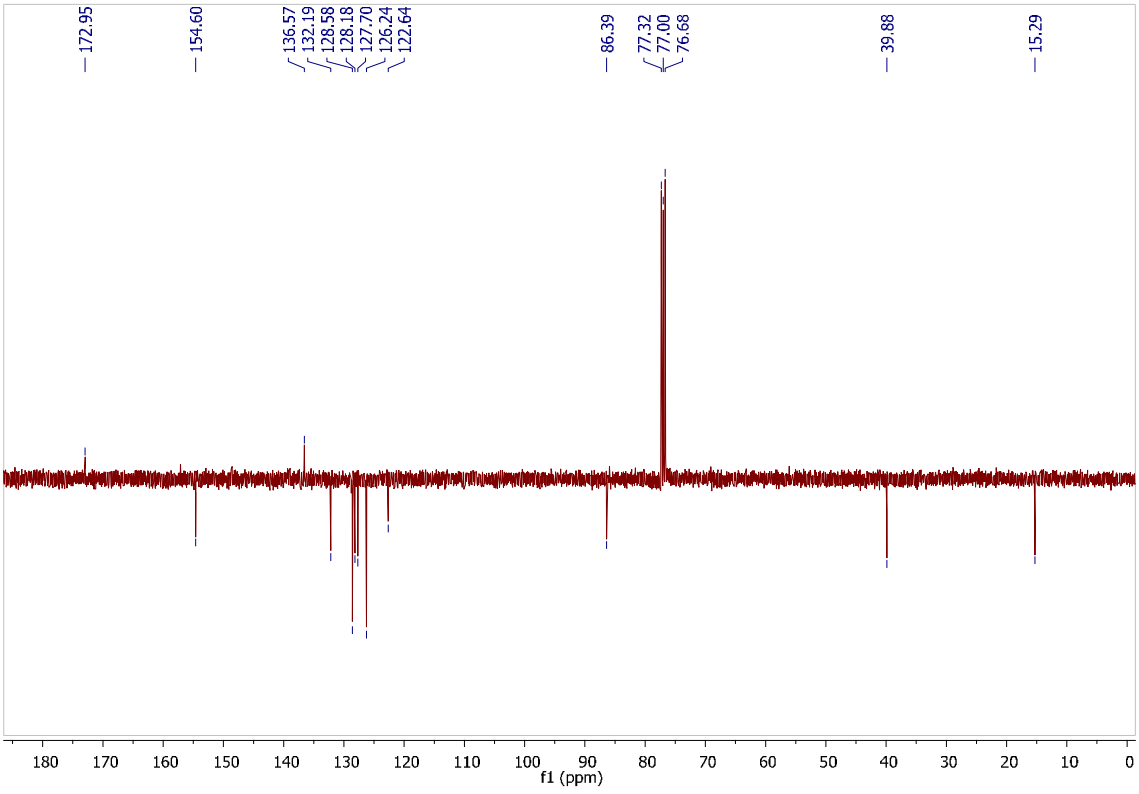
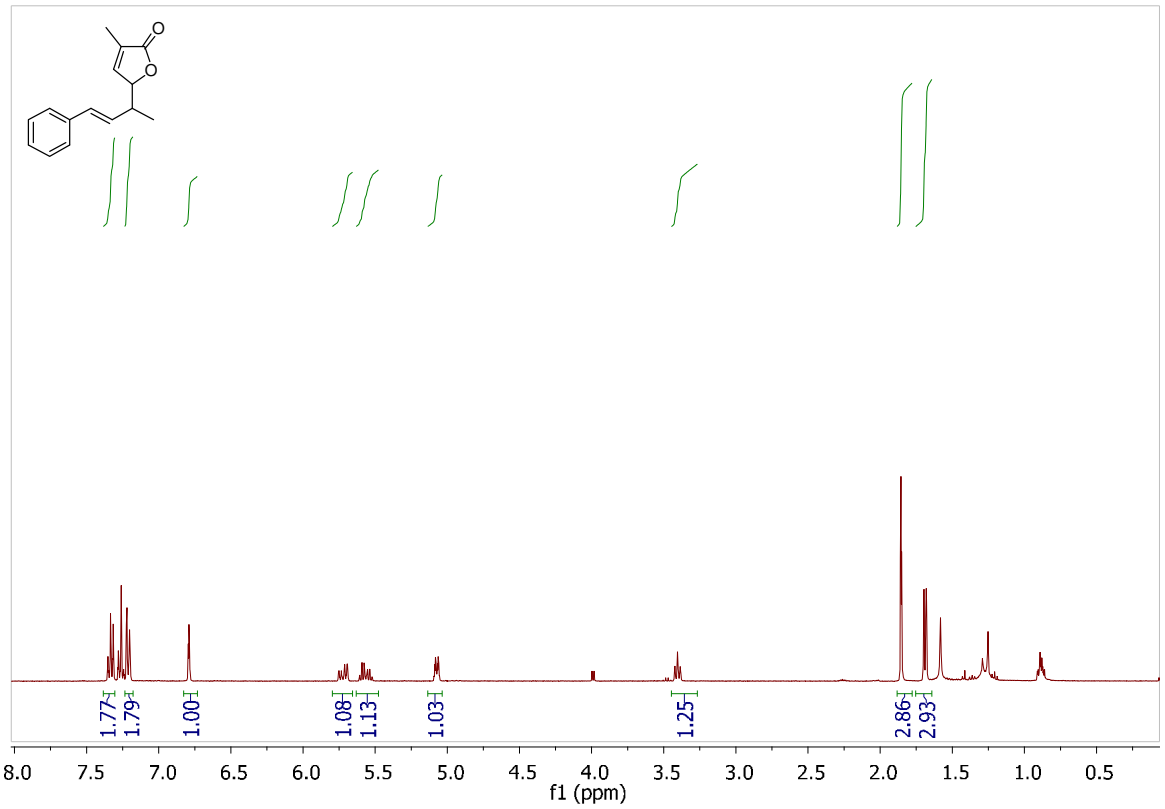
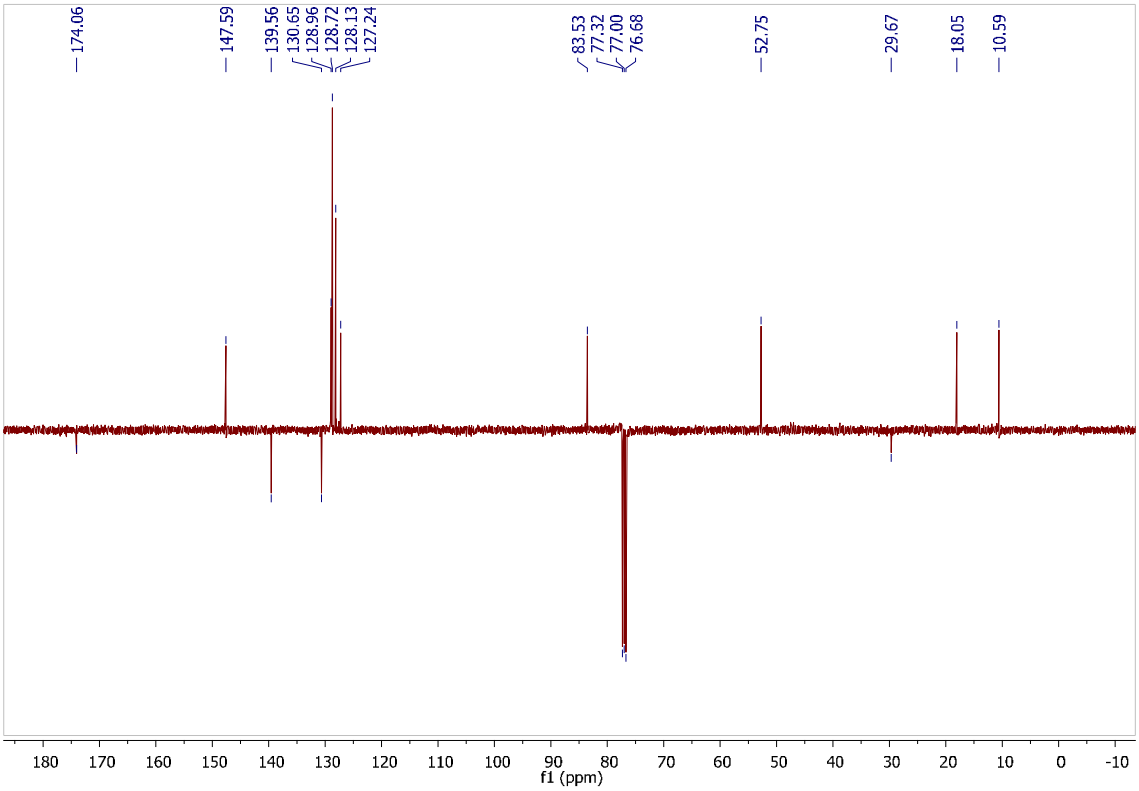


(-)-(*E*)-3-methyl-5-(4-phenylbut-3-en-2-yl)furan-2(5H)-one (5)

^{1}H-NMR

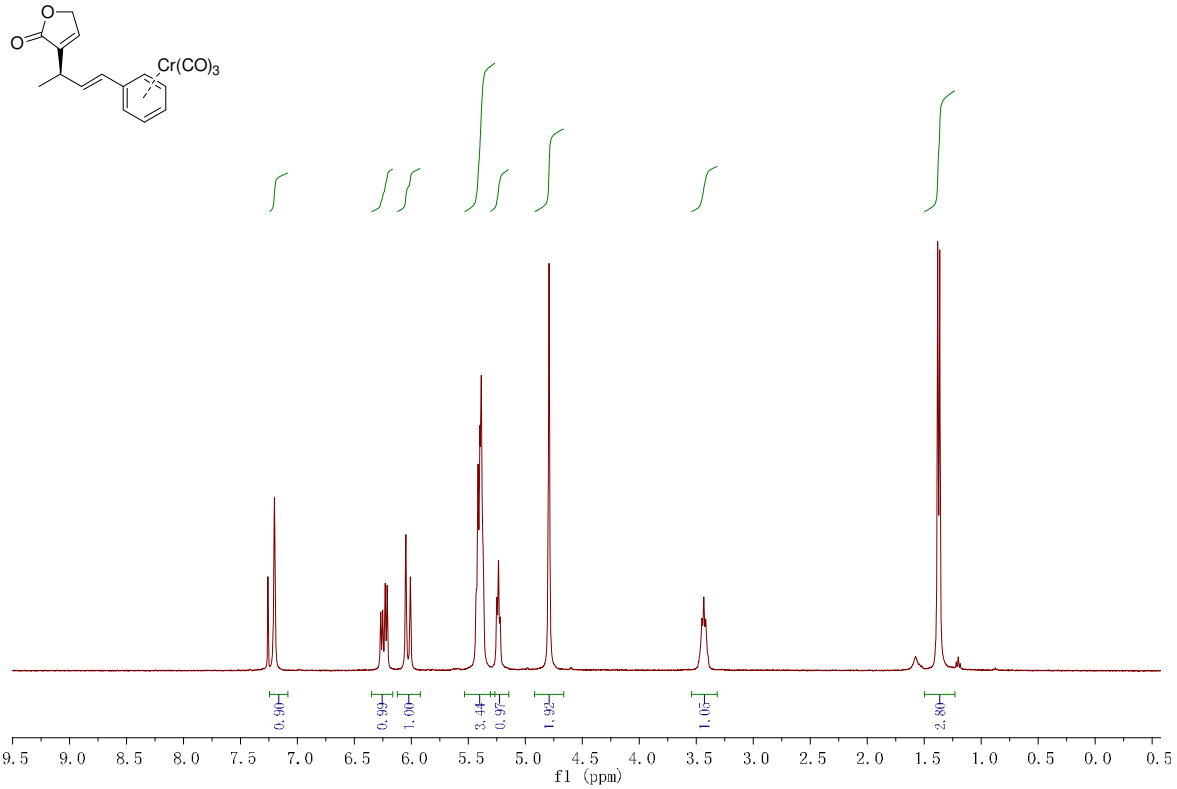


APT



Chromium Complex of 3c

^{1}H-NMR



^{13}C-NMR